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ASBESTOS/CEMENT PIPE CORROSION PART 2 – REVIEW OF RECENT WORK ON THE CAUSES OF PIPE DEGRADATION AND ON POSSIBLE IMPROVEMENTS

BORIS NEBESAR

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ASBESTOS/CEMENT PIPE CORROSION

PART 2 - REVIEW OF RECENT WORK ON THE CAUSES OF PIPE DEGRADATION AND ON POSSIBLE IMPROVEMENTS

by

Boris Nebesar*

ABSTRACT

Our current understanding of the theory of corrosion, explained in simple language, can provide the basis for improved control and prevention of corrosion of asbestos/cement pipe.

The environment, agents, and mechanisms of corrosion of asbestos/cement pipe are critically reviewed from the viewpoint of recent developments in basic knowledge and technology including use of different cements and protective coatings, changes in design of pipe and systems, control of transported drinking and waste water, use of bactericides, and removal of asbestos fibres. An executive summary and conclusions are given. This review is directed to a wide readership with various backgrounds and is based on 73 references in six languages, mainly from countries actively working on asbestos/cement pipe.

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CORROSION DES TUYAUX EN AMIANTE-CIMENT

DEUXIÈME PARTIE - ÉTUDE DU TRAVAIL RÉCENT SUR LA CAUSE DE LA DÉGRADATION DES TUYAUX ET LES AMÉLIORATIONS POSSIBLES

par

Boris Nebesar*

RÉSUMÉ

Notre compréhension actuelle de la théorie de corrosion, expliquée en termes clairs, peut servir de base pour un contrôle et une prévention améliorés de la corrosion des tuyaux en amiante-ciment.

Le milieu, les agents et les mécanismes de corrosion des tuyaux en amiante-ciment font l'objet d'une étude critique fondée sur des changements récents dans les notions de base et la technologie comprenant l'utilisation de différents ciments et revêtements protecteurs, les changements dans la conception des tuyaux et leurs systèmes, le contrôle de l'écoulement des eaux potables et effluentes, l'emploi de produits bactéricides et l'élimination des fibres d'amiante. Un résumé pour la direction ainsi que des conclusions sont présentés. Cette étude a été faite à l'intention de nombreux lecteurs de diverses disciplines et est fondée sur une documentation comprenant 73 références en six langues dont la plupart proviennent des pays qui effectuent actuellement des études touchant les problèmes des tuyaux en amiante-ciment.

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EXECUTIVE SUMMARY

Since ancient times the provision of clean water and safe sanitation has been one of the most basic concerns of civilized nations. Concurrently, the corrosion of the conduits has become a concern because of structural, economic and health reasons.

Asbestos/cement (A/C) pipe has provided these basic services reliably and inexpensively during several decades for tens of millions of people. However, because of recent concern about the hazards of asbestos, its possible effects through ingestion with water are scrutinized; so far without conclusive evidence of being harmful.

Much new knowledge concerning the problem inherent in the use of A/C pipe has been recently generated. Its corrosion, and that of other cement-bonded materials, is subject to the same physico-chemical laws as the degradation of rocks. New fundamental knowledge within the discipline of aquatic chemistry led to a new understanding of the degradation processes and therefore to possibilities for controlling or preventing them. This review surveys recent developments in the corrosion of A/C pipe.

CORROSION

For corrosion of any material, water must be present. Corrosion agents can attack A/C pipe from an aqueous, solid or gaseous environment. In most cases this involves natural, drinking, waste, or sea water which may act directly or from a (solid) soil. Gases, e.g., carbon dioxide, usually act through an aqueous phase.

A number of corrosion agents attack A/C pipe: acids (pH <6), sulphates, magnesium salts, alkaline hydroxides, ammonia (all at higher concentrations) and soft water (low calcium and carbonate). Some organic compounds are corrosive as well.

The corrosive action depends principally on the kind of agent, its concentration, duration of exposure, and convection conditions.

CORROSION MECHANISMS

The corrosion mechanisms involved in the degradation of A/C pipe are:

- Simple dissolution, governed by the solubility products of the constituents;
- Formation of soluble reaction products, e.g., after attack by some acids (hydrochloric, carbonic);
- Formation of expansive reaction products, e.g., gypsum and ettringite from sulphates or sulphuric acid;
- Microbiological conversions of sulphur in any valency state (S^0, S^{2-}, SO_4^{2-}) eventually leading to sulphuric acid and then finishing as previous case;
- Pressure of crystallizing salts, acting mechanically.

In all cases, the A/C matrix is disrupted and asbestos fibres can be released.

THEORY OF ASBESTOS/CEMENT PIPE CORROSION

The predominant mechanism of degradation is attack by soft water. Only recently has it been correctly explained in theory on the basis of chemical thermodynamics and related solubility of cement constituents.

In nature, the acidity (pH) of waters regulates biological life within narrow limits. All waters contain at least fundamental ions: the cations - hydrogen and calcium - and the anions - hydroxyl, carbonate and acid carbonate. Their concentrations are not arbitrary. If an imbalance exists for given conditions, either a dissolution or precipitation of calcium carbonate must correct the imbalance. Carbon dioxide from the atmosphere dissolves in water, and ubiquitous calcium rocks serve as a source of calcium. Complex mass and energy flows follow the established physico-chemical laws.

Exactly the same phenomena take place in A/C pipe. If calcium is deficient in the water, pipes are used as a source of calcium, resulting

in their degradation. Therefore, it is possible to assess the pipe condition from pH and bulk-chemical analysis of water, and from solubility diagrams of the compounds involved.

CONTROL AND IMPROVEMENTS OF A/C PIPE CORROSION

To control the corrosion of A/C pipe, a considerable choice exists for compositional adjustments of the pipe itself and of the transported medium. Less can be done with the pipe's outside environment.

A/C MATRIX

Performance of pressure and waste water pipes, made with various cements, has been determined by long-term field tests. Unequivocally, the best pipes were made of high-alumina cements.

For pressure pipe, the next best was blast-furnace slag cement, superior to normal portland cements, and the worst were C_3A-free cements. Density is by far the most important anti-corrosive property of the A/C matrix. There was not much difference in performance between the normal and autoclave-cured pipes.

For waste water pipes, high-alumina cements in formulations increased the life time fivefold over that with ordinary portland cement. Autoclave-cured pipes performed better than normal-cured.

On the basis of theoretical considerations, the performance of asbestos in A/C matrix cannot yet be matched, particularly in highly automated pipe manufacturing. The key to its high performance is homogeneous distribution in the matrix.

PIPE COATINGS

The greatest experience and choice in pipe protection have been with internal and external coatings, which must be applied during manufacturing: oil bitumen, coal-tar (not for inside use), coal tar-epoxy, epoxy. All effectively protect the pipe for a very long time. They are also the best means of protection against corrosive outside environment, e.g., bacterial action on sulphur.

If destruction of the surface of smaller-diameter imbedded pipe is severe, only an in-place lining can be applied. Cement-mortar and calcite linings are used, applied mechanically.

DRINKING WATER TREATMENT

This is a long used and effective means of pipe protection. Although costly, it can prevent staggering costs from corrosion of systems. A thin film is deposited from water by continuous addition of a suitable chemical. Lime is used most often; it deposits calcium carbonate. New investigations have shown some zinc compounds to be a viable alternative. Some natural waters contain compounds of iron, manganese, and silicon, which form a protective film. All the techniques used must satisfy strict water quality requirements.

During conventional water treatment, asbestos fibres can substantially be removed from the finished water.

WASTE WATER TREATMENT

This treatment is more difficult, because a great mixture of possibly corrosive agents can be present in waste waters. A total approach is necessary; system planners, designers and builders, and system-operating personnel must cooperate closely in all phases of the operation. Particularly corrosive agents in waste water are abundant sulphur compounds, which are transformed by bacterial action into sulphuric acid. Management of movement and of aeration is more important than chemical treatment, which is used as a last resort. If required, technical oxygen is the best means of treatment.

1. INTRODUCTION

To use or not to use asbestos has become a serious, world-wide societal issue. Speakers from many disciplines tried to resolve it at a recent world symposium on asbestos held "with a view to drawing up as objective and complete as possible an analysis of the asbestos situation" (1). However, the symposium perhaps raised more questions than it answered, while some acute problems of the use of asbestos-based products were not resolved.

Asbestos/cement (A/C) pipe is one such product. It is used worldwide and on a large scale, in particular for transport of drinking and waste water. Part 1 of this review presents the background to the problem of corrosion of A/C pipe (2).

In a recent report on leaching of an A/C material, Anderson and Stone stress that: "researchers have learned a great deal about asbestos-cement deterioration in water. However this information has not reached standard handbooks and manuals" (3). Apparently there is a problem of dissemination of the available information and its timely application.

In spite of all the computerized data bases, there is still no substitute for reviewing literature. Herring has shown that much more information relative to one's work is available today than previously, but this information must be made accessible through reviewing and used if we hope to resolve such complex problems as the corrosion of A/C pipe (Fig. 1-1) (4). Its solution requires contributions from many fields as Schock and Buelow have shown recently (5).

The corrosion of A/C pipe is not a new phenomenon, and those familiar with the pipe have always realized its potential danger from degradation. Therefore, they investigated mainly its mechanical and chemical resistance and also the safety and quality of the transported water long before the current efforts to resolve the question of ingested asbestos.

Many investigations, dating back to 1930, have been made of the successful field performance

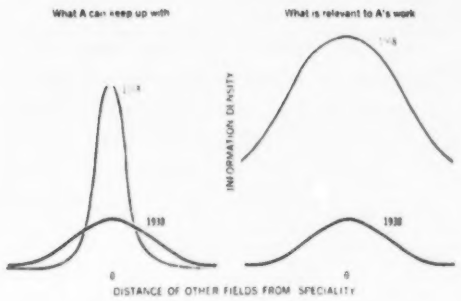


Fig. 1-1 - Distribution of information.
Left, various fields of information that "A" can keep in contact with. Right, information relevant to "A's" work (4)

of A/C pipe, as Huenerberg and Tessendorff summarized (6). Denison and Romanoff reported on an extensive, and later often quoted, investigation of the effect of exposure to soil on the properties of A/C pipe (7).

Because of the staggering economic losses, if for no other reason, the corrosion of water-transporting pipe has always been of concern. Merrill and Sanks reported estimated losses for the USA at $375 million annually, which could have been avoided if lime worth only ~7% of this sum had been used for stabilizing corrosive waters (8).

In late 1960, the concern about the effects of asbestos on health started. In the UK, investigations on the effects of inhaled asbestos led to the banning of crocidolite (9). At about the same time, several groups, including the manufacturers of A/C pipe, started detailed investigations on the presence of asbestos in drinking water. Cunningham and Pontefract (10), and Quint (11) reported their findings in 1971. In 1974, Kay gave detailed field data on the amounts of asbestos fibres found in all of Ontario's surface waters and concluded: "The Ministry of Health of Ontario indicated that ingestion of asbestos at these levels does not appear to present a health hazard. Research will have to continue, parti-

cularly to ascertain if there is a level of ingested asbestos that must not be exceeded" (12).

At the same time, the American Water Works Association Research Foundation reported in their detailed study of the problem of asbestos in water that "Such evidence as there is does not indicate any risk [...increased risk of cancer from asbestos present in water,...]" (13). The foundation planned specific long-term objectives in medical and technological domains to resolve questions regarding the occurrence of asbestos in drinking water systems, standardization of methods for determining asbestos, behaviour of A/C pipe and laboratory and field tests of pipe.

As a result of the increased effort, many data became available, such as surveys of drinking water in 71 Canadian municipalities (14), reported also by Toft et al (15), and over 1500 analyses of water in the USA, reported by Millette et al (16). These data confirmed that a small proportion of tested waters (~5% in Canada and ~15% in USA) did have an above-average content of asbestos fibres. In addition to natural sources, their origin was in a number of cases traced to A/C pipe.

The combined results of laboratory and field measurements started to show that the standardized aggressiveness index (AI) used to predict the behaviour of the A/C pipe was not reliable under unknown conditions. Buelow et al have observed conditions where water was either more or less aggressive than the AI predicted (17). The same conclusion was reached by Kanarek et al, who found that a nominally non-aggressive water released large amounts of asbestos fibres from the A/C pipe during transit (18).

The contributions from many groups and new basic knowledge, particularly in the new field of aquatic science that is itself unifying a number of disciplines, have led Schock and Buelow to a new theoretical explanation of the behaviour of A/C pipe (5). It will undoubtedly lead as well to a re-evaluation of much of our thinking about concrete under corrosive conditions.

In Part 2 of this study the environments, causes and mechanisms of corrosion, recent theoretical explanations, and some improvements for its control are reviewed.

Multilingual references are considered in general up to the end of 1981, with some later additions*. A/C pipe is used extensively in non-English-speaking countries where valuable contributions have been made to understanding its problems and to its technology. This knowledge, however, has often remained untapped because of language barriers.

In reviewing, one draws entirely on the work of others. The work of the following authors was consulted most often: Anderson and Stone (3), Schock and Buelow (5), Huenerberg and Tessendorff (6), Buelow, Millette, McPharen and Symons (17), Eick (19,20), Carrière (21), Marks and Hutchcroft (22), Neveux (23), Franquin (24), Stumm and Morgan (25), Lea (26), Grohmann (27), Anon. C E O C O R Study (28), Crennan, Simpson and Parker (29), Schock, Logsdon and Clark (30), Halleux and Bhatnagar (31).

2. CORROSION OF ASBESTOS/ CEMENT PIPE

2.1 CORROSION ENVIRONMENTS

The corrosion of A/C pipe takes place in a complex environment. Waters of various types can act on internal or external surfaces, soils in contact can be dry or moist at times, air can be absent or present. All constantly change with nature's forces and time; therefore, these corrosion environments are described briefly.

2.1.1 Water

Water is the predominant substance at the earth's surface. Without it there is no life and also no corrosion. Indeed, biological life stops outside a narrow range of pH. Therefore, the pH of most natural waters is from 6 to 9.

Halleux and Bhatnagar have summarized the main characteristics of natural water with

*The manuscript was submitted in December 1982 as Division Report MRP/MSL 82-141(R); Mineral Sciences Laboratories, CANMET, Energy, Mines and Resources.

respect to its composition (3). Apart from the chemical individuum of water, three main categories of substances are present: suspended, dissolved, and dissociated matter.

An important category of suspended matter is asbestos or asbestiform minerals. These are present in many natural waters from erosion, transfer through the atmosphere, or from industrial activities such as mining. In drinking water, asbestos may be found additionally under certain conditions after transport through A/C pipes or using incorrect tapping procedures (16).

The principal materials dissolved in natural water are gases (oxygen, carbon dioxide etc.), but small amounts of many substances, including organic matter, are dissolved as well.

Dissociated matter exists in two forms; as cations and anions. Only in these forms can matter react, this being substantially different from dissolved matter. Natural water always contains the fundamental cations H^+, Ca^{2+} and anions OH^-, HCO_3^-, CO_3^{2-}. The water is called "ideal water" if only these ions are present. More often, other ions, called "characteristic" ions, are present in various amounts. The cations are Mg^{2+}, Na^+ (K^+) and the anions are SO_4^{2-}, Cl^-, (NO_3^-). Their presence and quantity characterize the type of water.

Although there is only one substance defined as water, it is convenient for operational purposes to divide water into several categories.

2.1.1.1 *Natural water*

Natural water is often called fresh water. It originates from precipitation and acquires a characteristic composition while in contact with the surface and subsurface of the earth. Neveux categorizes waters in seven classes, with additional sub-classes, according to their characteristic content of substances (23). Table 2-1 summarizes their hardness and mineralization.

The majority of natural waters form an open system with the atmosphere.

2.1.1.2 *Drinking water*

When natural water is finished or is directly fit for human consumption, it is called drinking water. Great differences exist in practice, but generally included in this category is water which has been suitably finished, has the required quality within the prescribed limits, and is distributed by transporting through suitable pipes, i.e., in a closed system under pressure so that it is fully amenable to control. Table 2-2 gives the composition of drinking water and a summary of recommended limits (33). Table

Table 2-1 - Classification of natural waters (23)

No.	Water characteristics	Hardness French degree*	Mineralization mg/L approx.
1.	Very soft and no mineralization	0-3	0-50
2.	Soft and low mineralization	4-12	40-120
3.	Medium hard and light mineralization	14-35	120 -500
4.	Considerably hard and unstable mineralization	40-65	500-1000
5.	Extremely hard and strong mineralization; abnormal or accidental waters	60-120	>1000
6.	Soft and appreciably mineralized	few	varying but always very notable
7.	Artificially softened; if not additionally treated, very aggressive		

* 1 French degree = 10 mg $CaCO_3$/L

Table 2-2 - Composition of drinking water: summary of recommended limits (32)

Parameter	Maximum acceptable concentration*	Objective concentration*	Basis**
Aldrin + dieldrin	0.0007	$\leq 5 \times 10^{-8}$	H
Antimony	-	≤ 0.0002	H
Arsenic	0.05	≤ 0.005	H
Asbestos	-	-	-
Barium	1.0	≤ 0.1	H
Boron	5.0	≤ 0.01	H
Cadmium	0.0005	≤ 0.001	H
Carbaryl	0.07	$\leq 5 \times 10^{-4}$	H
Chlordane (Total)	0.0007	$\leq 5 \times 10^{-8}$	H
Chloride	250	< 250	A
Chromium	0.05	≤ 0.0002	H
Colour (TCU)	15	< 15	A
Copper	1.0	< 1.0	A
Cyanide	0.2	≤ 0.002	H
DDT (Total)	0.03	$\leq 5 \times 10^{-8}$	H
Diazinon	0.014	$\leq 1 \times 10^{-6}$	H
Dieldrin + aldrin	0.0007	$\leq 5 \times 10^{-8}$	H
Endrin	0.0002	$\leq 5 \times 10^{-8}$	H
Fluoride	1.5	1.0***	H&A
Hardness	-	-	-
Heptachlor + heptachlor epoxide	0.003	$\leq 5 \times 10^{-8}$	H
Iron	0.3	< 0.05	A
Lead	0.05	≤ 0.001	H
Lindane	0.004	$\leq 1 \times 10^{-7}$	H
Manganese	0.05	< 0.01	A
Mercury	0.001	≤ 0.0002	H
Methoxychlor	0.1	$\leq 5 \times 10^{-8}$	H
Methyl Parathion	0.007	$\leq 1 \times 10^{-6}$	H
Nitrate (as N)	10.0	≤ 0.001	H
Nitrilotriacetic Acid (NTA)	0.05	≤ 0.0002	H
Nitrite (as N)	1.0	≤ 0.001	H
Odour	-	Inoffensive	A
Parathion	0.035	$\leq 1 \times 10^{-6}$	H
Pesticides (Total)****	0.1	-	H
pH	6.5-8.5	-	A
Phenols	0.002	< 0.002	A
Selenium	0.01	≤ 0.002	H
Silver	0.05	≤ 0.005	H
Sodium	-	-	-
Sulphate	500	< 150	H&A

Table 2-2 - cont'd

Parameter	Maximum acceptable concentration*	Objective concentration*	Basis**
Sulphide(as H_2S)	0.05	<0.05	A
Taste	-	Inoffensive	A
Temperature(°C)	15	<15	A
Total dissolved solids	500	-	A
Total organic carbon	-	-	-
Toxaphene	0.005	$\leq 5 \times 10^{-8}$	A
Trihalomethanes	0.35	$\leq$0.0005	H
Turbidity (NTU)	5	<1	H&A
Uranium	0.02	$\leq$0.001	H
Zinc	5.0	<5.0	A
2,4-D	0.1	$\leq$0.001	H
2,4,5-TP	0.01	$\leq$0.001	H

* Unless indicated otherwise, the maximum acceptable and objective concentrations are specified in mg/L.

** Maximum acceptable and objective concentrations have been established on the basis of either aesthetic (A) or health (H) considerations.

*** In areas where the annual mean maximum temperature is below 10°C, the objective is 1.2 mg/L.

**** The "total pesticides" limit applies to water in which more than one of the pesticides listed in this Table is present, in which case, the sum of their concentrations should not exceed 0.1 mg/L.

Note:
"Asbestos: There is insufficient information on which to base a maximum acceptable concentration for asbestos in drinking water. Asbestos may be introduced into natural waters by the dissolution of asbestos-containing rocks and from industrial effluents. The use of asbestos-cement pipe in the distribution systems of public water supplies may contribute to the asbestos content of potable water. In addition, although few quantitative data are available, food is a significant source of asbestos ingested by humans. Exposure to airborne asbestos is a well-documented health hazard; similar evidence of a health risk associated with exposure to asbestos by ingestion has not been found."

2-3 lists the composition of a variety of typical drinking waters (27). For now, only the last three columns are of interest, showing the pH, the concentration of calcium, and the ionic strength, which is a measure of all contained ions.

2.1.1.3 *Waste water*

Waste water is much more complex than drinking water or even natural water. In this category we include (city) sewage and a great variety of industrial waste waters. Crennan et al list different types of sewages in Table 2-4 (29).

Waste waters are transported in pipes either under artificial pressure, or gravity. In the latter the liquid may have an open surface. Due to its widely varying composition, waste water is more difficult to control than drinking water.

Table 2-3 - Analyses of a cross-section of waters at a pH value with SI = 0 (waters in calcium-carbon dioxide equilibrium) (27)

		m-value mmol/L	p-value mmol/L	Q_e mmol/L	Ca^{++} mmol/L	μ* mmol/L	pH with SI = 0 20°C
1	Tübingen	6.8	-1.3	8.1	5.5	25	6.90
2	Mannheim (Freudenheim)	6.1	-0.9	7.0	3.6	14	7.05
3	München	5.8	-0.3	6.1	2.15	10	7.26
4	Berlin	3.85	-0.2	4.05	1.85	10	7.49
5	Bodenseewasserversorgung	2.50	-0.1	2.6	1.25	5	7.75
6	Hannover (North)	1.85	-0.08	1.93	1.5	7	7.84
7	Frankfurt (Schwanheim)	1.63	-0.08	1.71	0.6	3	8.21
8	Siegburg (Wahnbachtalsperre)	0.78	+0.02	0.75	0.58	3	8.57
9	Frankfurt (Spessart)	0.47	+0.03	0.44	0.2	1	9.20
10	Harzwasserwerke (Okertalsperre)	0.32	+0.04	0.28	0.22	1	9.41

* μ is the ionic strength of water to which all ions contribute.

Table 2-4 - Types of sewages (29)

1. Normal fresh domestic sewage, without trade wastes, in gravity and pressure sewers.
2. Sewage containing mineral acids or organic acids derived from food wastes.
3. External or internal exposure to groundwater containing aggressive CO_2 or neutral sulphates.
4. Sewage containing excessive grease or fat.
5. Septic sewage containing H_2S flowing through gravity sewers and pressure mains.

2.1.1.4 *Sea Water*

The bulk of water on earth is sea water. It has a particular composition which is remarkably stable and unobtainable by evaporating natural water.

The average salt composition of sea water is given by Franquin (24):

NaCl	27 g/L
$MgCl_2$	4
$MgSO_2$	1.7
K_2SO_4	0.9
$CaSO_4$	1.3
$Ca(HCO_3)_2$	4.15

Apart from these salts, which may be directly involved in corrosion, there are microorganisms present that also affect the corrosion process.

2.1.2 Soil

A/C pipes are usually underground in integrated systems. The earth or, interchangeably called the ground, soil or terrain, supports the pipes, but it may also interact with the external surface. Actually, the water in or from soil is the corrosion vehicle. Neveux has described the influence of soils on pipelines (23).

Soils are defined as the surface layers of terrain formed from decomposed rocks and by other processes; they are suitable for agriculture, whereas the subsoil is not. Soils consist of rocky, sandy, clay or calcareous layers, all forming so called "good" or "bad" soils from the viewpoint of corrosion and all being continuously renewed and transformed by physical, chemical and biological actions.

The physical characteristics of soil include its petrological nature, granulometry, porosity, humidity, apparent density, pH, resistivity and redox potential. A pipeline's trace is also influenced by topographical, geographical, geological, botanical, biological and electrical features.

Corrosion depends mainly on the amount of water a soil is capable of retaining. That in turn depends on the porosity of a soil, which is defined as the ratio of volume of voids to the apparent density for a given mass. The apparent density of soils is generally from 1.4 to 2.0; organic matter reduces it. The diameter of pores and the nature of constituents determine, by capillary action and absorption, the capability of soil to retain water. Depending also on the climate and permeability of the subsoil, all moisture levels from dry to wet can exist.

The chemical properties of soil depend on its soluble and insoluble constituents. The latter, composed of various oxygenated compounds, form the mineral framework. Although calcium carbonate is generally insoluble, it dissolves in the presence of carbon dioxide. The red or brown colour of soils indicates higher iron oxides, grey suggests a lower oxidation state, and black an accumulation of organic matter.

The principal soluble constituents of soils are the cations of hydrogen, sodium, potassium, magnesium and calcium, and the anions of carbonate, acid carbonate, nitrate, chloride and sulphate. Of these, hydrogen, chloride and sulphate increase the aggressivity of water, while calcium decreases it by its buffering action.

One must differentiate between the soil water, held in soil, and the soil extracts, drained from soils after extraction.

An important characteristic of soils is their acidity. It originates from the action of water on soil, ion exchange, presence of humic matter, type of surface vegetation, biological life and the circulation of carbon dioxide. There are two measures of acidity, not directly correlatable. The pH is a measure of initial intensity of attack and is influenced by buffering effects, e.g., of humic acids while the total (titratable) acidity gives the absolute aggressivity as the complete reserve in hydrogen ions.

Biological characteristics of soils originate from organic matter, which is the remnants of vegetation and animals present particularly in surface layers of all soils. Their decomposition along the carbon, nitrogen and sulphur cycles produces corrosive compounds. The reactions are most dangerous in soils, because an intense bacterial activity accompanies them. It is impossible to enumerate all bacteria and microorganisms, but there are hundreds of millions of bacteria in just 1 cm^3 of soil. We differentiate between the aerobic bacteria, requiring oxygen and thriving in light aerated soil, and the anaerobic bacteria, needing no oxygen and proliferating in heavy compacted soils. Their number and activity depends on seasonal humidity and temperature.

From a practical viewpoint the most aggressive soils and those exhibiting the greatest corrosion danger, are compact clayey, peaty soils, with high soluble salt content, mostly humid and poorly aerated. Fortunately, the A/C pipe is non-metallic and non-conductive and therefore is not subject to corrosion based on electrochemical and oxidation phenomena. Nevertheless, there is no absolutely non-aggressive soil or completely protective coating; so the corrosion can only be slowed down, not stopped. The choice of route for the proposed pipeline through the different types of soils present is therefore most critical.

2.1.3 Air and Gases

A/C pipe is also used for the transport of air and coal gas in both aboveground and underground conduits. Gases from air, particularly carbon dioxide, are very important for the corrosion process, although they may not act directly.

An example of coal gas composition (in ppm) is given below (33):

pH	- 6.7	Aliphatic hydrocarbons	- 74
CO_2	- 1474	Unsaturated hydrocarbons	- 193
H_2S	- 7	Ketones	- 430
Mercaptans	- 279	Nitrites	
NH_3	- 130	Organic acids	
HCN	- 33	(aliphatic)	- 721
HCNS	- 31	Phenols:	
SO_4	- 225	monohydroxy	- 153
Nitrogen bases		polyhydroxy	- 1050
With NH_2 groups	- 150	Aminophenol	- 872
All alcohols	- 378	Acid amides	- 18

Here also, the gas acts on A/C via the condensate rather than directly, but the main transported medium is gaseous.

2.2 CORROSION AGENTS ATTACKING ASBESTOS/CEMENT PIPE

Little can be added to the authoritative, detailed compilation by the CEOCOR of corrosion agents that attack A/C pipe (28). The translated summary is reproduced in Table 2-5. For now, only the first column is of interest.

Much of the compilation is based on the experimental work of Eick (19) who, as a member of the CEOCOR Editorial Committee, has translated the report into German (34). Huenerberg and Tessendorff also reported the experimental results (6).

Apart from listing recognized corrosion agents such as inorganic and some organic acids, sulphates, carbonic acid, magnesium salts, soft water, ammonia and hydroxides, the guide gives valuable information about the less-recognized corrosiveness of some organic compounds.

Another compilation of corrosive agents is presented in Table 2-6, from the American Concrete Institute (ACI) Manual (35). Although it is intended for concrete, the information is valuable for studying corrosion problems of the A/C matrix, which is likewise a cement-bonded material.

2.3 CORROSION MECHANISMS

Corrosion of practically all materials is an ancient problem. A/C pipe has been no exception, because all materials based on hydraulic binders are subject to corrosion.

Early observations were linked with the metallic and concrete piping then used for the distribution of water. All had some corrosion problems because of safety (lead, zinc, copper), impaired water quality (iron), or mechanical resistance (concrete and iron). It was natural to seek solutions to problems of corrosion analogous to the approaches and experience with the known materials. Only slowly did a full understanding of the mechanisms of the corrosion of A/C matrix emerge.

Franquin gives some basic philosophy about the corrosion of concrete: it is the consequence of chemical phenomena between the environment and the cement stone, and physical phenomena that permit the penetration of aggressive fluids into the mass (24). Water is indispensable for the reactions and transport of aggressive agents. The evolution of corrosion phenomena varies, depending on alternating humidity and dryness, which either accelerate or retard it. Temperature and ambient variations, repeated leaching by sea and pure waters, and salt encrustations may all contribute to corrosion. There is no general rule.

In a recent example of these premises, Helms and McCoy showed how wrong conclusions were reached on the corrosive action of sulphate on A/C pipe when presupposing that intermittent wet-dry exposure would be more destructive than a continuous one. Just the reverse was true (36).

According to Eick (19), Huenerberg and Tessendorff (6), and the CEOCOR study (28) the corrosion-related properties of A/C material are considerably different from those of its metallic and concrete counterparts. A/C has a low electrical conductivity and thus is not subject to electrochemical corrosion due to the formation of corrosion cells, or to errant currents that require extensive protection in metal piping. Neither oxygen nor hydrogen attack A/C, and it resists attack by plant roots and bacteria.

A/C differs from metals and concrete in that corrosion progresses and softens the matrix in only a thin surface layer from tenths to a few millimetres deep [Huenerberg and Tessendorff (6), Quint (11), Eick (19)]. Because bulk concrete is permeable, corrosion agents can diffuse into its matrix which is therefore more susceptible to degradation than the A/C matrix. The degradation products of concrete are known to be harmless to humans, while this is still being questioned for A/C. Eick notes that asbestos fibres in the A/C pipe matrix are resistant to practically all corrosion phenomena (19). Huenerberg and Tessendorff (6) state that in the presence of bases, chrysotile yields products which resist chemical attack; however, Riedel et al have found by measurement of properties of asbestos fibres that after one year of exposure in a solution saturated with calcium hydroxide (pH 12.48), their tensile strength decreased by 43.4%, their modulus of elasticity de-

Table 2-5 - Asbestos/cement pipe: limits of concentration [of corrosive agents] for a temperature $\leq 25°C$ and continuous service (28)

Designation	No protection	External protection	Internal protection			
Type of coating	-	Coal tar	Oil bitumen	Coal tar	Tar epoxy	Epoxy
pH	≥ 6	≥ 4.5	≥ 4.5	≥ 4.5	≥ 3.5 (*)	≥ 3.5(*)
Titrated acidity mL NaOH (N/10)/100 g of soil	<20	<30	-	-	-	-
Hardness in French degrees	>5	no limit	no limit	no limit	no limit	no limit
CO_2 aggressive: mg/L CO_2	(**)	<30 mg/L	<30 mg/L	<30 mg/L	no limit	no limit
SO_4 = mg/L as a function of Cl mg/L	Cl mg/L / SO_4 mg/L	no limit	no limit	no limit	no limit	no limit
portland cement with 8 to 10% C_3A	0 / <500 3000 / <800 5000 / <1430					
NH_4 = mg/L	<80	no limit	no limit	no limit	no limit	no limit
MgO = mg/L as a function of SO_4 mg/L	SO_4 mg/L / MgO mg/L	no limit	no limit	no limit	no limit	no limit
	0 / <2000 200 / <700					
Alkaline hydroxydes	< 10%	no limit	no limit	no limit	no limit	no limit
Vegetable and animal oils mg/L	<300	no limit	<300	no limit	no limit	no limit

Table 2-5 - cont'd

Designation	No protection	External protection	Internal protection			
Type of coating	-	Coal tar	Oil bitumen	Coal tar	Tar epoxy	Epoxy
Lower alcohols and non-polar solvents:						
- Esters-waxes-fatty acids-alkaline soaps	does not resist	does not resist esters	does not resist esters	does not resist esters	does not resist esters	does not resist esters
- Benzene-toluene-xylene	no limit	no resistance of coating	no resistance of coating	no resistance of coating	no resistance of coating	no resistance of coating
Higher alcohols and polar solvents:						
- Glycol-glycerine-acetone	does not resist	does not resist	does not resist	does not resist	does not resist	does not resist acetone
- Phenol mg/L	<70	≤1000	≤1000	≤1000	≤10 000	no limit
- Sugar	practically not attacked	no limit	no limit	no limit	no limit	risk estimated as a function of pH
In case of fermentation with production of CO_2 and acetic lactic acids	does not resist	risk estimated as a function of pH	risk estimated as a function of pH	risk estimated as a function of pH	risk estimated as a function of pH	

*Tolerates occasionally and for short periods increased acid concentrations

**Because of complexity of equilibrium for soft waters: inquire from manufacturers

creased by about 34%, and elongation at fracture was reduced by 13.2%, (the latter with poor precision) (37).

Barbakadze et al reported that the corrosion of asbestos fibres in acidic environments starts at pH <3 (38). Opoczky and Pentek found that magnesium can be slowly extracted from chrysotile, at least during exposure to the atmosphere (39). Efforts to understand the mechanisms of corrosion of the A/C matrix have always concentrated on its cement component; therefore the available knowledge about other cement-based matrices can be applied or at least used as a basis for A/C work. Many factors affect corrosion, regardless of the individual mechanism, but the most important are (6,19,28): the kind of corrosion agent; concentration of the corrosion agent; duration of its action; and convection conditions in the reaction environment. Other factors are: volume of the transported medium; velocity of the transported medium; temperature; water content (for ionization and transport); solubility of the reaction product; composition of material's protective surface layer.

2.3.1 Dissolution of Constituents

Dissolution is the simplest type of corrosion mechanism and a number of A/C constituents are subject to it. The governing factor is the solubility product, which is a constant for a given compound and conditions at a particular temperature. For calcium carbonate,

$$K_{SO} = \{Ca^{2+}\} \{CO_3^{2-}\}$$

The thermodynamic notation with brackets represents ion activities which may be considered to be an idealized concentration. The latter is often used in approximations, but then it is necessary to express the true activities with additional coefficients.

When the ion product for the given compound exceeds the value of K_{SO} the compound will be deposited; when it is smaller than K_{SO} the compound will dissolve, and only when the ion product equals the solubility product will the system be at equilibrium. It is obvious that in complex natural systems the last condition is seldom, if ever, achieved.

Free lime is the most soluble constituent in A/C paste. Its role in durability of cement-based matrices has been well documented (26). Equally well known is the solubility of calcium carbonate in water, of hydrated calcium silicates, and to a certain degree, of alumina (Fig. 2-1) (3). All constituents may be soluble however, even if to a miniscule degree. In a strictly thermodynamically evaluated system, this must be considered.

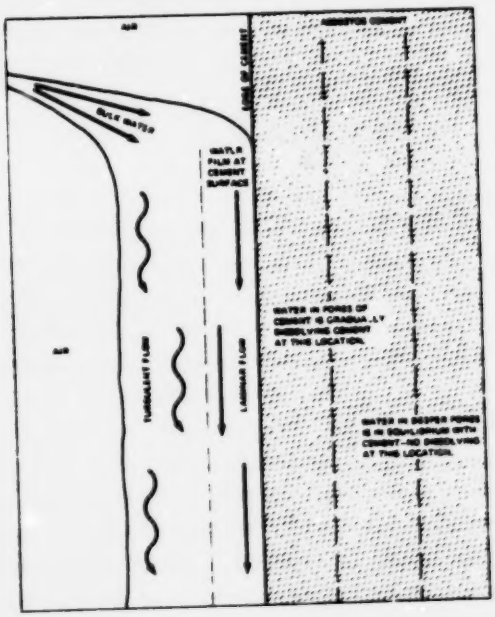


Fig. 2-1 - Dissolution of calcium compounds in water. Water flow over asbestos-cement fill. Water is slightly undersaturated with respect to calcium carbonate (3)

2.3.2 Reactions Yielding Soluble Products

The best known reactions of this type are with the hydrogen ion, which usually originates from various acids. It is necessary to differentiate between intensity factors, expressed as pH, and an acid or base-neutralizing capacity, determined only by titration.

Because of buffering actions in solutions, it is possible that a weak acid of higher pH will be corrosive for a long time, due to constant replenishment of spent acid from a large reservoir of $[H^+]$, whereas a relatively strong acid might be less corrosive. Some organic acids

Table 2-6 - Effect of commonly used chemicals on concrete (35)

Rate of attack at ambient temperature	Inorganic acids	Organic acids	Alkaline solutions	Salt solutions	Miscellaneous
Rapid	Hydrochloric Hydrofluoric Nitric Sulphuric	Acetic Formic Lactic	-	Aluminum chloride	-
Moderate	Phosphoric	Tannic	Sodium Hydroxide- >20%*	Ammonium nitrate Ammonium sulphate Sodium sulphate Magnesium sulphate Calcium sulphate	Bromine (gas) Sulphite liquor
Slow	Carbonic	-	Sodium hydroxide 10-20%* sodium hypochlorite	Ammonium chloride Magnesium chloride Sodium cyanide	Chlorine (gas) Seawater Softwater
Negligible	-	Oxalic Tartaric	Sodium hydroxide <10%* Sodium hypochlorite Ammonium hydroxide	Calcium chloride Sodium chloride Zinc nitrate Sodium chromate	Ammonia (liquid)

* Avoid siliceous aggregates because they are attacked by strong solutions of sodium hydroxide

that are common in soils often react in this manner.

In the CEOCOR study the sources of acidity have been listed as follows (28):

- hydrothermal waters, volcanic activity
- humic acids, resulting from biological decomposition of vegetation
- certain bacteria (Section 2.3.4)
- industrial waters, refuse, garbage
- industrial pollution, with an elevated content of sulphur dioxide that produces acid rain.

Acids react with the constituents in the surface layer of A/C pipe and, in relation to the depth of softening, the physical and chemical properties change. The structure weakens and may eventually decompose, but there is no expansion.

The solubility of the reaction products has a great influence on the rate of corrosion. Eick has shown in Fig. 2-2 that an acid yielding an insoluble product, such as calcium sulphate, will corrode A/C much less than an acid yielding a completely soluble product such as calcium chloride (19). It will be even less destructive than a buffer having a considerably higher pH. The reason is that the protective gypsum layer, formed in the surface portion of the A/C decreases the rate of corrosion by sulphuric acid because of a change from convection to diffusion of the corrosive agent. In later stages, gypsum begins to decompose. Many organic acids in soils that form salts which are difficultly soluable, act in a similar manner.

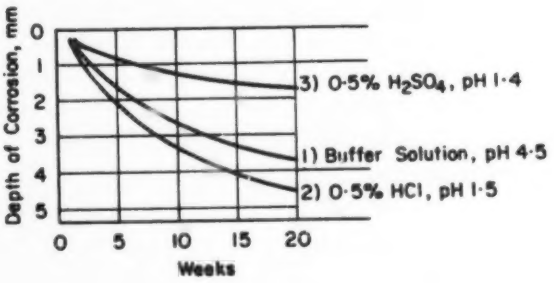


Fig. 2-2 - Influence of contact time on the depth of corrosion (19)

Acids decompose A/C at pH <6. Extensive recommendations with respect to soil acidity, water movement, presence of sulphates, and allowable pH are given by the ASTM (40).

The action of carbonic acid, a weak acid, produces a special kind of corrosion. Carbon dioxide is produced mostly by respiration and photosynthesis, as well as from the following sources (28):

- combustion gases, industrial exhausts, automobile exhausts
- volcanic activity
- hydrothermal waters
- bacterial decomposition of organic matter

Decades of work and effort have been spent understanding the reactions of carbonic acid in general and of its corrosive action in particular. Lea has presented its interactions with cement-based materials (26). Only recently, however, has its role in nature been elucidated more precisely within the discipline of aquatic science. Stumm and Morgan have described these developments (25). The new concepts have drastically changed our current understanding of the behaviour of carbon dioxide and disposed of the ingrained, but now outdated, concepts of "free" and "aggressive" carbonic acid. Grohmann has summarized in Table 2-7 the critical remarks and alternatives to Tillmans earlier terminology of calcium-carbonic acid equilibrium (41).

2.3.3 Reactions Yielding Expansive Products

The expansion and the degradation of cement-based matrices resulting from interaction with sulphate-carrying waters and soils have been extensively researched and amply documented. They are covered in the standard works of Lea (26), the ACI Manual (35), Huenerberg and Tessendorff (6), are reported by Eick (19), Franquin (24), and are included in the CEOCOR study (28).

Apart from primary matter, sulphates originate from the oxidation of sulphur dioxide, SO_2, principally, from garbage dumps, refuse, volcanos, industrial activity, and combustion gases of many kinds. Discharge to the atmosphere produces acid rain. Their microbiological origins are described separately in Section 2.3.4.

There is no danger of internal corrosion of A/C pipe from transported drinking water having a maximum limit of 250 ppm sulphates. However, it is different for the external surface, sometimes exposed in very aggressive sulphate-bearing soils, and in particular for sewer pipe, carrying potentially high concentrations of sulphur compounds. Various authorities permit different levels of sulphates, indicating disagreement as to their effect. Sulphates are generally present in the environment. Under favorable conditions in a solution they combine with calcium ions, mostly derived from lime, to form expansive salts: first gypsum and later ettringite formed from it and hydrated tricalcium aluminate. The reaction takes place in a neutral or alkaline medium at 40-80°C, with a large increase in volume that causes inter-

Table 2-7 - Critical remarks and alternatives to Tillmans' terminology of calcium-carbonic acid equilibrium (41)

$CaCO_3.aq + CO_2.aq = Ca(HCO_3)_2.aq$	Unproven working hypothesis of the 19th century. ($CaCO_3$) solid is dissolved in the normal way in water (as a strong electrolyte), yielding Ca^{2+} and CO_3^{2-} ions. The CO_3^{2-} ions are subject to pH-buffering (Fig. 3-2)
"Belonging carbonic acid"	No compound in a chemical sense, "Calculated equilibrium concentration of the free carbonic acid" "calculated CO_2 - required value"
"Excessive carbonic acid" "Deficient carbonic acid"	No compound in a chemical sense. "Deviation from the CO_2 equilibrium concentration" "Nominal value-deviation of the free carbonic acid" "Tillmans - indicator" "CO_2 - indicator"
"Aggressive carbonic acid" "Lime-aggressive carbonic acid" "Metal-aggressive carbonic acid" "Rust-protection prohibiting carbonic acid"	Terms without a chemical or physical content.

nal pressure and disruption. Gypsum first retards the progress of corrosion, but in later stages, monocalcium and tricalcium sulphoaluminates are formed.

The exact mechanism of the formation of this salt is also disputed. According to Franquin, the reaction product can be either crystalline, formed from solution as in supersulphated cements which resist cracking, or it can be a powder reacting as a solid that expands because of its voluminosity (24). Tricalcium aluminate goes into solution only if free lime in the aqueous phase is low.

Magnesium sulphate acts disruptively because of its reactions with lime, hydrated calcium silicates, aluminates, and calcium sulphoaluminates. Precipitation of magnesium hydroxide is favoured, whereas gypsum is formed with calcium.

The case of sea water is interesting as discussed by Franquin, because it contains high concentrations of both sulphates and magnesium (24). However, chloride is present in high concentration as well, which increases the solubility of other salts and in particular retards the formation of ettringite. The result is lesser corrosion than in comparable sulphated groundwaters. The formation of a carbonated surface (from carbonates in solution) acts as a barrier to the penetration by sulphates, and to the leaching of lime from the matrix. Microorganisms present partially block the pores, and the additional deposi-

tion of magnesium hydroxide in pores completes a very successful formation of a resistant surface.

Although these reactions apply to concrete, A/C with its much denser structure behaves even better, as described for the Genova system (2) and documented by Huenerberg and Tessendorff for the sea water-carrying systems (6).

2.3.4 Microbiological Conversions of Sulphur

Sulphur is a most ubiquitous element in nature. It is an important part of the biota, where in the sulphur cycle various bacteria transform it by various means into a number of forms. The final corrosion agents formed belong to the two previously discussed classes: sulphuric acid and sulphate. They can attack both the external and internal surfaces of pipe. An intermediate form is hydrogen sulphide, a highly poisonous, explosive and odorous gas. The concentration of hydrogen ions from it is not sufficiently high for it to act as an acid by itself, but it is further transformed to corrosive compounds.

In the microbiological field, a generalized scheme for transformation has evolved. Figure 2-3 gives various reaction paths and compounds obtained (42). A summary that includes other steps is given in Fig. 2-4.

Figure 2-5 (43), gives a scheme of the action of hydrogen sulphide, and in Fig. 2-6 a "niche" for sulphur-oxidizing bacteria is depicted (44). In Table 2-8, conditions for the formation of sulphuric acid are summarized (20).

Table 2-8 - Factors leading to the formation of sulphuric acid in open-level area (20).

- H_2S concentration	:	>0.5 ppm in gas space
Odour threshold	:	0.1 ppm
Maximum allowable concentration	:	10 ppm
- Presence of H_2S-oxidizing bacteria (Thibacillus concretivorus, multiplication optimum at ~28°C)		
- Condensate on the open-level pipe-wall (no transformation on dry pipe-walls)		
- Aeration of the open-level deficient (H_2S concentration increases)		
- Temperatures from 10 to 50°C (above and below the oxidation rate decreases noticeably) therefore warm climates with little dilution-water are the most favourable conditions.		

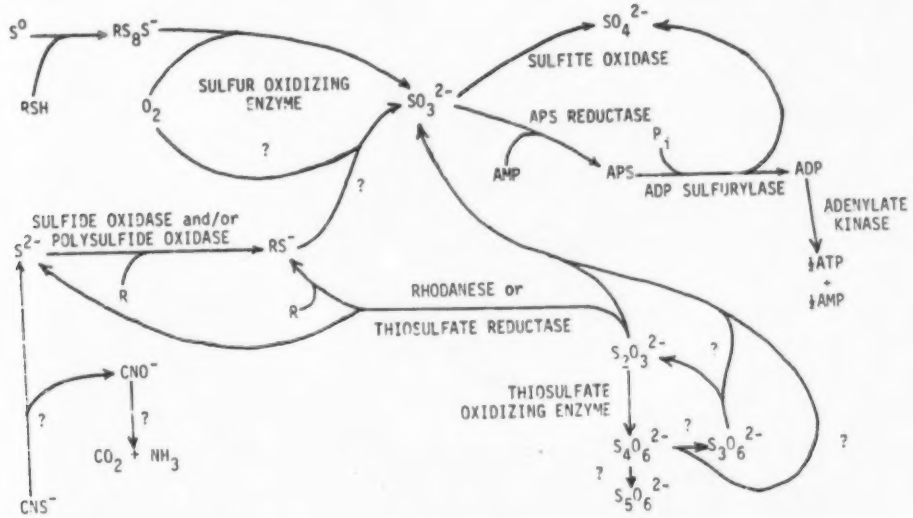


Fig. 2-3 - Generalized scheme for the oxidation of elemental sulphur and reduced sulphur compounds by thiobacilli (42)

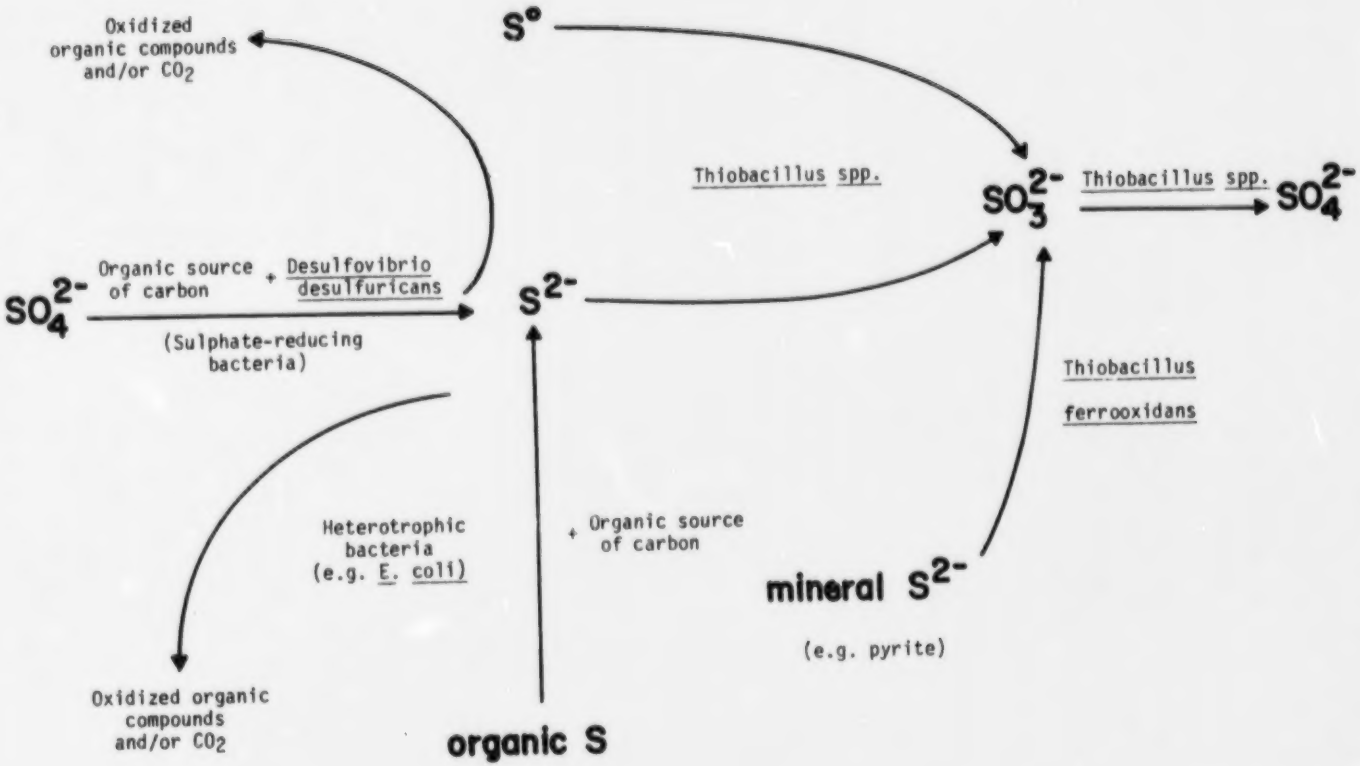


Fig. 2-4 – Summary of microbiological sulphur-transforming steps

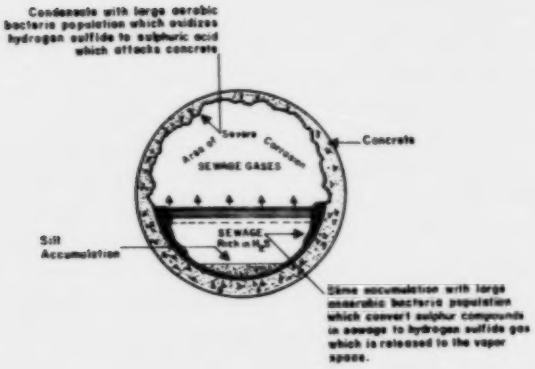

Condensate with large aerobic bacteria population which oxidizes hydrogen sulfide to sulphuric acid which attacks concrete
Area of Severe Corrosion
Concrete
SEWAGE GASES
SEWAGE
Back in H_2S
Silt Accumulation
Slime accumulation with large anaerobic bacteria population which convert sulphur compounds in sewage to hydrogen sulfide gas which is released to the vapor space.

Fig. 2-5 - Cross-section of concrete sewer pipe under typical corrosive conditions (43)

The range of acidity in which thiobacilli operate is:

Bacterium	pH
T. thiooxidans	2-4
T. ferrooxidans	2-4
T. thioparus	6-8
T. novellus	7-9

The formation of hydrogen sulphide from organic compounds can be either aerobic or anaerobic, depending on the environment, and the species will grow as required. Thiobacilli found particularly in sewers are *T. concretivorus* (20) and *T. neapolitanus* (29).

Recently, Koenig and Stoelting reported their gas-chromatograph mass-spectrometer (GC/MS) determinations of compounds present in samples of highly corrosive waste water and the overlying atmosphere (45). Prior to their GC/MS determinations they did not detect hydrogen sulphide either by smell (limit 1×10^{-3} mg/L) or by the sensitive lead acetate test. Concentrations of hydrogen sulphide were <1 mg/L. Contrary to this, massive corrosion of concrete by sulphuric acid was progressing, and they were able to identify trithiapentane (CH_3-S-S-S-CH_3) in waste water and the easily volatilized diethylsulphide $(C_2H_5)_2S$ in the atmosphere. They propose that the thiobacilli can either exist on very low concentrations of hydrogen sulphide or, alternatively, microorganisms can metabolize other vola-

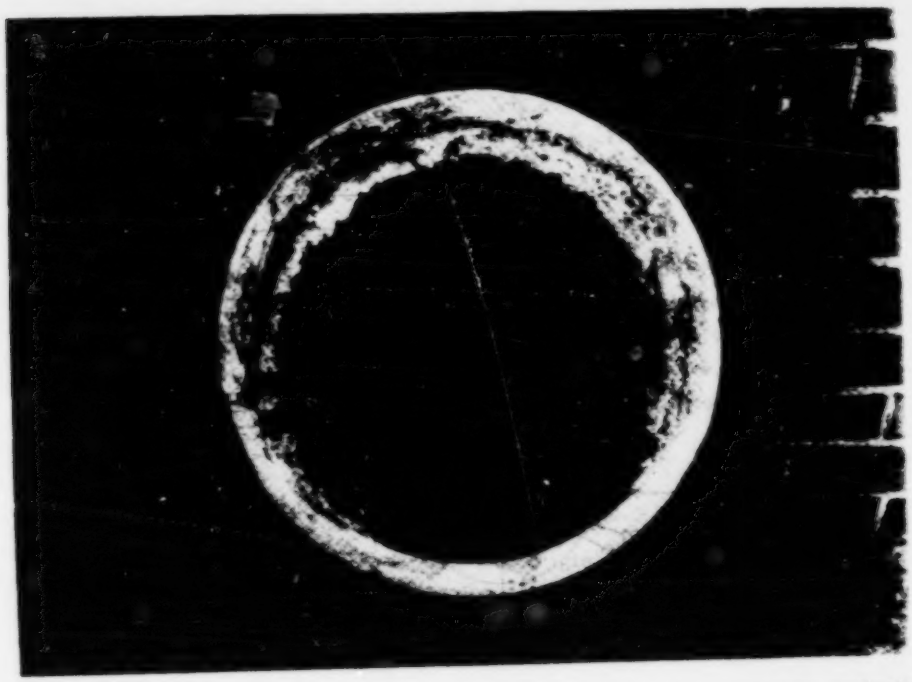


Fig. 2-6 - Formation of a "social niche" from A/C fibres by microorganisms producing sulphuric acid (44)

tile sulphur compounds. If the latter is valid the widely accepted mechanism of formation of sulphuric acid from hydrogen sulphide will have to be reconsidered.

The corrosion problems related to septic sewage are particularly acute in hot climates (46).

2.3.5 Pressure of Crystallizing Salts

A/C corrosion in soils caused by crystallization of salts takes place on the external surfaces of pipes in cyclical dry-moist conditions and on internal surfaces with changing level of the transported medium. Crystals of various salts, e.g., alkali sulphates and carbonates, crystallize in pores of the structure during evaporation or migration of water and disrupt the pipe matrix mechanically. Potassium salts have a low surface tension and are particularly subject to creeping.

Cyclical dry-wet conditions at the sea surface are thought to be the harshest encountered in nature. Therefore, long-term field testing of corrosion is often performed on the sea coast to establish the durability of materials; because of its smooth surface and dense, low-porosity structure, A/C is subjected to this corrosion mechanism less than concrete (6).

3. THEORITICAL EXPLANATION OF ASBESTOS/CEMENT PIPE CORROSION

3.1 pH AS A MASTER VARIABLE - ROLE OF CARBON DIOXIDE - ROLE OF CALCIUM

The ultimate aim of work on corrosion is to prevent it or control it. This is not possible without understanding its complexities. The corrosion of A/C pipe is, as are all corrosion phenomena, essentially related to the characteristics of the waters causing the deterioration.

Stumm and Morgan have shown in their text on aquatic chemistry that we must treat the behaviour of even an enormously complex system such as the earth in a strict theoretical way (25). The science most useful to us in this is chemical thermodynamics because the system "earth" behaves according to established physico-chemical laws. The interaction, dissolution and deposition of matter on earth follows the weathering cycles of rocks associated with water, shown in Fig. 3-1 (25). The water-borne acids from the interior of the earth act on the bases at the earth's surface and cause continuous weathering of the rocks. The biosphere is involved through its many cycles, such as those of carbon, sulphur, nitrogen and phosphorus. All biological life, and indeed the weathering process, is governed by the activity

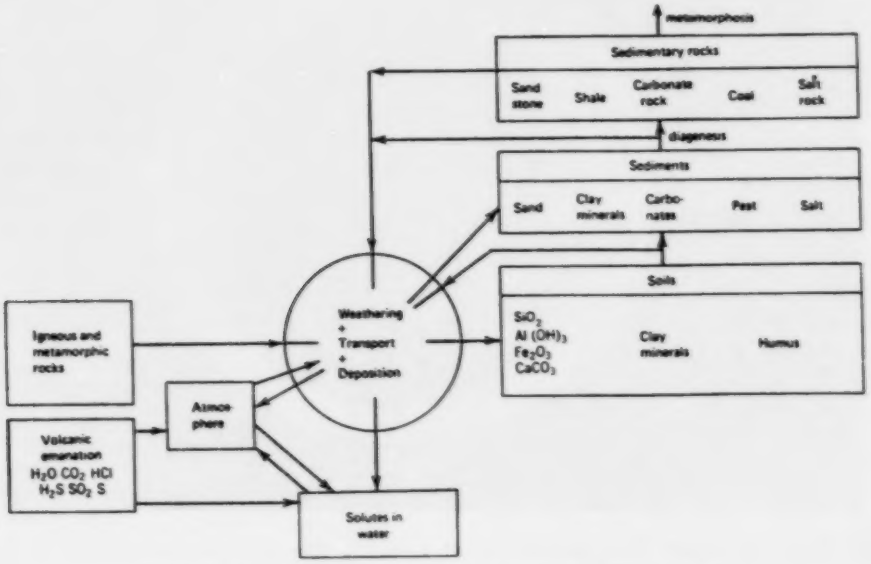


Fig. 3-1 – Interaction of the cycle of rocks with that of water (25)

of the hydrogen ion (H^+); thus, the pH of waters is a main variable in organic and inorganic reactions.

The reasoning follows the now well established BrØnsted theory, classifying acids as proton donors and bases as proton acceptors. Water has the ability for self-ionization (autoprotolysis):

$$H_2O + H_2O = H_3O^+ + OH^-$$

and is thus an inexhaustible source of protons. In a dilute aqueous solution $(H_2O) = 1$, and the equilibrium constant for the reaction, usually called the ion product of water, is:

$$K_w = (OH^-)\ (H_3O^+) = (OH^-)\ (H^+)$$

At 25°C, $K_w = 1.008 \times 10^{-14}$ and the pH = 7.00, corresponding to exact neutrality in pure water where $[H^+] = [OH^-]$. K_w changes with temperature.

The governing factor for the concentration of protons is carbon dioxide, whatever the source. But for it to react the presence of calcium ions is necessary, as presented in Table 3-1 (41). Calcium carbonate is ubiquitous in nature; its dissolution or precipitation, according to its solubility product governs the interactions because the concentrations of fundamental ions are not arbitrary.

The fundamental change in our understanding, important in particular for the control of drinking water and therefore having an influence on the corrosion of A/C pipe, is the strict

Table 3-1 - Scheme of interaction between solid calcium carbonate and ions Ca^{2+}, CO_3^{2-}, HCO_3^- and free carbonic acid (41)

$(CaCO_3)$ solid $\overset{H_2O}{\rightleftharpoons}$ Ca^{2+} + $CO_3^{=}$	Origin from Ca-containing minerals and chemicals, e.g., calcite, dolomite, gypsum, lime milk, lime water.
H_3O^+ ⇅ HCO_3^- + H_2O $(CO_3^{2-} \rightleftharpoons HCO_3^- + OH^-)$	Origin from inorganic-C-containing minerals and chemicals, e.g., soda-ash, calcite, dolomite, magnesite, Na-hydrogen-carbonate.
H_3O^+ ⇅ $H_2CO_3 + H_2O$ $(HCO_3^- \rightleftharpoons H_2CO_3 + OH^-)$ $H_2CO_3 \rightleftharpoons CO_2 \cdot aq$	Origin from atmospheric and from conversion CO_2 of matter.

Table 3-2 - Equilibrium relationship of fundamental ions (31)

$H_2O \rightleftharpoons H^+ + OH^-$	$K_w = (H^+)(OH^-)$	(0)
$H_2O + CO_2 \rightleftharpoons H^+ + HCO_3^-$	$K_1 = \frac{(H^+)(HCO_3^-)}{(CO_2)(H_2O)}$	(1)
$HCO_3^- \rightleftharpoons H^+ + CO_3^{=}$	$K_2 = \frac{(H^+)(CO_3^{=})}{(HCO_3^-)}$	(2)
$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{=}$	$K_s = (Ca^{2+})(CO_3^{=})$	(3)
$(CO_2)_T = (CO_2) + (HCO_3^-) + (CO_3^{=})$		(4)
$2(Ca^{2+}) + (H^+) = (OH^-) + (HCO_3^-) + 2(CO_3^{=})$		(5)

application of the solubility product for calcium carbonate and the understanding of its dissolution by carbon dioxide. For decades, the reaction was interpreted as:

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$$

It is no longer valid today. Now, the interpretation is that calcium carbonate dissolves directly (as does an ionic compound) and its solubility depends on the solubility product (Equation 3 in Table 3-2).

This difference has resolved all the difficulties with the concept of aggressive, free, bound etc. carbon dioxide, as given in Table 2-7. It made obsolete all diagrams and indices previously devised for its measurement, as Neveux (23), and Anderson and Stone (3), respectively, have described them.

Sources of protons in addition to autoprotolysis of water are:

dissociation of strong acids $HCl + H_2O \rightarrow H_3O^+ + Cl^-$

dissociation of weak acids, e.g., carbonic $H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-$

Biological reactions exert a strong influence on pH. Oxygenation in general reduces it, and sulphate reduction as well as denitrification increase it, as seen in Section 2.3.4.

All reactions in all systems, however complex, proceed on the basis of general physiochemical laws controlling:

- proton balance (electroneutrality),
- mass reactions,
- solubility products of all involved species, and
- ion product of water.

To solve the proton balance equation, there must be available as many equations as there are interactions.

Halleux and Bhatnagar have presented the equilibrium relationships for fundamental ions (Table 3-2) (31). Their evaluation depends on the availability of the necessary constants and on bulk-solution analytical determinations. An example of the necessary data has been given in Table 2-3.

These fundamental changes in our knowledge have in a decisive way contributed to the theoretical understanding of the corrosion of A/C pipe, as Schock and Buelow recently reported (5). For their computer-assisted modelling of saturation indexes and precipitation diagrams, developed as a new tool for the following of chemical equilibria in complex systems, they used the aqueous reactions given in Table 3-3 and the solid reactions given in Table 3-4. From this concurrent pilot-plant and field work they concluded that A/C pipe is a safe and durable product, if constraints on the quality of water, based on its

Table 3-3 - Aqueous reactions considered in the construction of the Saturation Index and precipitation diagrams (5)

Reaction	log K†	Source
Hydrogen		
$H^+ + OH^- = H_2O$	14.00	1
$2H^+ + CO_3^{2-} = H_2CO_3$*	16.7	2
$H^+ + CO_3^{2-} = HCO_3^-$	10.3	3
$2H^+ + CO_3^{2-} = CO_2(g) + H_2O$	18.14	2
$H^+ + PO_4^{3-} = HPO_4^{2-}$	12.4	4
$2H^+ + PO_4^{3-} = H_2PO_4^-$	19.6	4
$3H^+ + PO_4^{3-} = H_3PO_4^o$	21.7	4
Calcium		
$Ca^{2+} + H_2O = CaOH^+ + H^+$	-12.6	5
$Ca^{2+} + CO_3^{2-} = CaCO_3^o$	3.2	5
$Ca^{2+} + CO_3^{2-} + H^+ = CaHCO_3^+$	11.3	5
$Ca^{2+} + H^+ + PO_4^{3-} = CaHPO_4^o$	15.1	5
$Ca^{2+} + 2H^+ + PO_4^{3-} = CaH_2PO_4^+$	20.3	5
$Ca^{2+} + PO_4^{3-} = CaPO_4^-$	6.5	5
Magnesium		
$Mg^{2+} + H_2O = MgOH^+ + H^+$	-11.8	5
$Mg^{2+} + CO_3^{2} = MgCO_3^o$	3.0	5
$Mg^{2+} + CO_3^{2-} + H^+ = MgHCO_3^+$	11.4	5
$Mg^{2+} + H^+ + PO_4^{3-} = MgHPO_4^o$	15.3	5
Sodium		
$Na^+ + CO_3^{2-} = NaCO_3^-$	1.2	5
Zinc		
$2Zn^{2+} + H_2O = Zn_2OH^{3+} + H^+$	-9.0	1
$Zn^{2+} + H_2O = ZnOH^+ + H^+$	-9.0	1
$Zn^{2+} + 2H_2O = Zn(OH)_2^o + 2H^+$	-16.9	1
$Zn^{2+} + 3H_2O = Zn(OH)_3^- + 3H^+$	-28.4	1
$Zn^{2+} + 4H_2O = Zn(OH)_4^{2-} + 4H^+$	-41.2	1
$Zn^{2+} + H^+ + PO_4^{3-} = ZnHPO_4^o$	15.6	4
$Zn^{2+} + 2H^+ + PO_4^{3-} = ZnH_2PO_4^+$	21.2	4
$Zn^{2+} + CO_3^{2-} = ZnCO_3^o$	4.8*	6
$Zn^{2+} + H_2O + Cl^- = ZnClOH^o + H^+$	-7.5	7
$Zn^{2+} + Cl^- = ZnCl^+$	0.4	4
$Zn^{2+} + 2Cl^- = ZnCl_2^o$	0.6	4
$Zn^{2+} + 3Cl^- = ZnCl_3^-$	0.5	4
$Zn^{2+} + 4Cl^- = ZnCl_4^{2-}$	0.2	4
Iron		
$Fe^{3+} + H_2O = FeOH^{2+} + H^+$	-2.2	1
$Fe^{3+} + 2H_2O = Fe(OH)_2^+ + 2H^+$	-5.7	1
$Fe^{3+} + 3H_2O = Fe(OH)_3^o + 3H^+$	-13.6	1
$Fe^{3+} + 4H_2O = Fe(OH)_4^- + 4H^+$	-21.6	1
$2Fe^{3+} + 2H_2O = Fe_2(OH)_2^{2+} + 2H^+$	-3.0	1
$3Fe^{3+} + 4H_2O = Fe_3(OH)_4^{5+} + 4H^+$	-6.3	1
$Fe^{3+} + H^+ + PO_4^{3-} = FeHPO_4^+$	17.8	5
$Fe^{3+} + Cl^- = FeCl^{2+}$	1.4	5
$Fe^{3+} + 2Cl^- = FeCl_2^+$	2.1	5
$Fe^{3+} + 3Cl^- = FeCl_3^o$	1.1	5

†All data are for 25°C

*The published data of Bilinski et al have been reinterpreted by Schock et al in terms of both $ZnCO_3^o$ and $Zn(CO_3)_2^{2-}$ with log K = 5.2 for $ZnCO_3^o$ and with log K = 7.5 for the reaction: $Zn^{2-} + 2CO_3^{2-} = Zn(CO_3)_2^{2-}$. These constants were incorporated into the model after the calculations were performed.

Table 3-4 - Solid reactions considered in preparation of Saturation Index diagram (5)

Reaction	log K+	Source
Calcium		
$Ca^{2+} + CO_3^{2-} = CaCO_3(s)$	8.5	1
$Ca^{2+} + 2H_2O = Ca(OH)_2(s) + 2H^+$	-22.8	2
$Ca^{2+} + H^+ + PO_4^{3-} + 2H_2O = CaHPO_4.2H_2O(s)$	18.9	3
$8Ca^{2+} + 6PO_4^{3-} + 2H^+ + 3H_2O = Ca_4H(PO_4)_3.3H_2O$	46.9	3
$5Ca^{2+} + 3PO_4^{3-} + H_2O = Ca_5(PO_4)_3OH(s) + H^+$	40.6	4
Magnesium		
$Mg^{2+} + CO_3^{2-} = MgCO_3(s)$	7.5	5
$Mg^{2+} + 2H_2O = Mg(OH)_2(s) + 2H^+$	-16.8	7
$3Mg^{2+} + 2PO_4^{3-} + 8H^+ = Mg_3(PO_4)_2.8H_2O(s)$	25.2	2
Zinc		
$Zn^{2+} + CO_3^{2-} = ZnCO_3(s)$	10.8	6
$5Zn^{2+} + 2CO_3^{2-} + 6H_2O = Zn_5(OH)_6(CO_3)_2(s) + 6H^+$	-9.7	6
$Zn^{2+} + 2H_2O = Zn(OH)_2(s) + 2H^+$	-12.5	7
$3Zn^{2+} + 2PO_4^{3-} + 4H_2O = Zn_3(PO_4)_2.4H_2O(s)$	35.3	8
Iron III		
$Fe^{3+} + 3H_2O = Fe(OH)_3(s) + 3H^+$	-4.9	5
$Fe^{3+} + PO_4^{3-} + 2H_2O = FePO_4.2H_2O(s)$	26.4	2

complex chemical behaviour, are maintained. If the transported water is undersaturated with respect to calcium, the calcium constituents present in pipe will be used to replenish it, leading to pipe deterioration. Remedial measures include in-field deposition of protective films from zinc compounds added to transported water. Similar films were sometimes observed in existing systems, even with aggressive water, but they are ineffective on substantially degraded pipe. The aggressivity index, currently used for assessing the corrosive quality of water, is not a reliable measure on theoretical grounds. The new theoretical views and tools are also directly applicable to other than A/C piping, in particular concrete.

4. CONTROL AND IMPROVEMENTS IN PREVENTION OF ASBESTOS/CEMENT PIPE CORROSION

The potential for corrosion of A/C pipe was realized when it was first used. When the pH of the media in contact drops <6, attention must be given to its control and to the application of corrosion prevention measures. These measures are sometimes designated as passive or active, or as being external or internal. They are classified as being related to the A/C pipe, to the transported medium and to the external environment.

4.1 CONTROL OF ASBESTOS/CEMENT PIPE TECHNOLOGY

The effect of the A/C matrix, the design parameters for the pipe, the protective coatings and linings, and the use of bactericides are reviewed.

4.1.1 Changes in the Asbestos/Cement Matrix

In this category the composition of the cement used, the A/C composite, and curing are discussed.

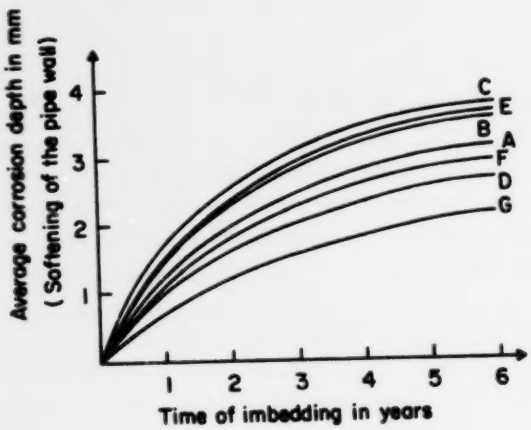
4.1.1.1 *Composition of cement*

Rigorous laboratory and field tests of A/C pipe manufactured with high alumina cement (HAC) have proven its corrosion resistance is superior to pipe made with any other cement.

For drinking water, Eick (20) has reported the results, shown in Fig. 4-1, of testing pipe with seven different kinds of cements under very aggressive carbonic acid conditions. The pipe made with HAC performed the best, followed by that made with blast furnace slag cement.

Analytical Data

- Lime-dissolving CO^2	100 mg CO^2/L (lime-dissolving capacity
- German carbonate hardness	10°
- Saturation Index	-1.8 (ΔpH to equilibrium)
Basis: CO^2 enriched	Berlin tap water.



Normal and autoclave-cured portland cement pipe performed less well and two C_3A-free cements performed the worst; their results bracketted those of iron-portland cement. The corrosion rate in all pipes dropped with time. In no case did the soft layer exceed 4 mm which indicates that the density of A/C pipe has more effect than the kind of cement used.

Excellent performance of experimental sewer pipe made with HAC was reported by Crennan et al (29). Seven kinds of cements were tested in sewers for five to eight years. Extensive laboratory and pilot-plant testing evaluated the resistance to neutral sulphate, sulphuric acid and gaseous hydrogen sulphide. A fivefold increase in life, compared with that of autoclaved pipe made with ordinary portland cement (OPC), was obtained. The life of A/C pipes made with supersulphated cement was two to three times longer and that with OPC two times longer than the life of equivalent concrete pipes. No silica was used in HAC formulations.

	Cement analysis						
Components	A	B	C	D	E	F	G
CaO	65.12	63.28	62.63				37.7
SiO_2	21.46	21.15	21.61				2.8
Al_2O_3	5.52	4.10	4.00				40.8
Fe_2O_3	2.12	6.39	6.70				18.0
MgO	0.76	0.99	0.95				0.5
SO_3	2.50	1.85	2.42				0.03
Ignit.loss	1.70	1.58	1.28	A + 70% blast furnace slag	A + 30% blast furnace slag	A + 40% quartz flour	-
Insol.	0.14	0.12	0.11				0.1
C_3S	60	60	54	-	-	-	-
C_2S	15	16	22	-	-	-	-
C_3A	11	-	-	-	-	-	-
C_4AF	6	19	20	-	-	-	-
Blast furnace slag	0	0	0	70	30	0	0

A: Normal portland cement
B: C_3A-free portland cement
C: C_3A-free portland cement
D: Blast furnace cement
E: Iron portland cement
F: A + SiO_2 steam-cured
G: Fused alumina cement

Fig. 4-1 - Corrosion by acid waters after 6-yr flow through unprotected pipes (20)

To resist sulphates, Huenerberg and Tessendorff (6) and the CEOCOR study (28) earlier suggested the use of cements with less than 3% C_3A, or containing 70% blast furnace slag. From static laboratory exposure tests, Barbakadze et al concluded that the best A/C performance is obtained with low-C_3S cements, not surpassing 50-52% (Table 4-1); they also had the highest content of C_4AF (38). These cements yielded samples of the highest density, lowest water absorption, and comparable strength.

Kuznetsova studied the influence of reducing or oxidizing atmospheres during cement calcination (47). She concluded that cements produced in a reducing atmosphere (Table 4-2), have a lower hydration rate because the microstructure is poor (Fig. 4-2). They also have lower filtrability for cement and A/C (Table 4-3),

Table 4-1 - Characteristics of starting cements and properties of A/C samples (38)

Cement plant	Mineralogical composition of cements in %				R bending kg/cm^2	W % (water abs.)	γ [density] g/cm^3
	C_3S	C_2S	C_3A	C_4AF			
Zdolbunovskii	59	19	7	13	307	20.2	1.76
Bekhabatskii	53	23	6	13	300	21.7	1.72
Akhangaranskii	48	27	4	16	298	19.2	1.83

Table 4-2 - Phase composition of clinkers, % (47)

Index of clinker sample	Results of analysis: Chemical C_3S	C_2S	C_3A	C_4AF+ glassy phase	X-ray: alite	Belite from β-C_2S	C_3A + +NC_3A_3	C_4AF
37-1	60	14	5	16	61	16	3.3	16
37-2	57	16	8	14	58	16	5	13.3
37-A-1	52	24	6	15	50	25	3.3	15.4
37-A-2	50	26	9	13	50	25	6.3	13.4
ChTsZ-1	57	14	5	16	57	15	5	16
ChTsZ-2	44	27	8	14	46	25	8.6	15

Table 4-3 - Filtration properties of cement and A/C mixtures (47)

Index of clinker sample	Cement: Volume of separated water, cm^3	R compression MPa	Density g/cm^3	Cement + asbestos: Volume of separated water, cm^3	R compression MPa	Density g/cm^3
37-1	1	2.2	2	7.7	3.53	1.7
37-2	0.9	2	1.9	4.5	3.03	1.5
37-A-1	1.2	2.1	2	7.7	4.24	1.6
37-A-2	1.0	1.6	1.9	4	2.83	1.5
ChTsZ-1	1.4	2.5	2.1	7.2	4.16	1.7
ChTsZ-2	1.C	2	1.9	4.5	2.4	1.5

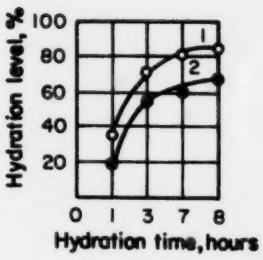


Fig. 4-2 - Hydration level of cements from X-ray analysis data:

(1) cement on the basis of clinker, calcined in oxydizing atmosphere;

2) same, in reducing atmosphere (47)

leading to a higher retention of water, which in turn slows down the compaction of A/C layers. Finally, a high-C_3A content reduces strength because of aluminate recrystallization. The phase changes in cement are particularly accentuated when A/C products are heated.

4.1.1.2 *Asbestos/cement composite*

The modern theory of fibre-reinforced concrete (FRC) has permitted a better understanding of the A/C composite. Hannant (48) described, among others, asbestos cement and de Mahieu (49) presented a highly mathematical treatment of the lesser-known theory, based on production experience. Thus, the long and difficult phenomenological development of A/C is now being completed with the explanation in retrospect of the theoretical basis of A/C performance, all leading to an improved practical use.

Krenchel reviewed FRC developments (Walton, 50), and concluded that expectations of mass production have not yet materialized, partly because asbestos fibre performance can not as yet be duplicated. Earlier, Krenchel listed six features of a successful FRC (51):

1. high-fibre content
2. ductile fibres
3. thin fibres
4. uniform fibre distribution
5. for 2-d orientation: maximum l/d
6. for 3-d orientation: optimum l/d

A uniform distribution is very difficult to attain with fibres other than asbestos because they cannot impart the same buoyancy to cement. A comparison with the theoretical requirements of fibres for FRC, set by Riedel et al and given below, shows that an even distribution of asbestos fibres in the matrix is the most important advantage for the A/C composite (37).

The general requirements of fibres for correct interaction with cement paste are (37):

- tensile strength higher than that of the binder,
- modulus of elasticity larger than or equal to that of the binder,
- low permanent elongation of the fibre,
- elongation at fracture larger than or equal to that of the binder,
- good bonding of the fibre to the cement paste, depending on: aspect ratio, chemical-mineralogical composition, anchoring depth, and shearing strength resistance of the fibre,
- non-reactive with water and binder,
- carrying capacity of fibres for the cement,
- good dispersion in the cement suspension,
- no fibre disintegration during preparation,
- hygienic - environmental suitability.

All classical texts on A/C (6,52) and recent reports (20,28,38) agree that a density of ≥ 1.78 g/cm^3, but preferably higher, is the most important protective measure against corrosion because it prevents intrusion of aggressive agents. High density is achieved by keeping the water/cement (W/C) ratio below 0.27 and by compacting well; it is also used as a quality-evaluation measure (38). Eick documented the resistance of A/C against sulphates in comparison to non-asbestos matrices (20) (Fig. 4.3). Corrosion attacks only the surface because a complex protective layer is formed by various compounds, notably hydrated cement gel and calcium carbonate. The layer increases its resistance with time. Recently however, Buelow et al (17) and Schock and Buelow (5) reported considerable attack on autoclave-cured A/C pipe even in mildly aggressive water because of silicate losses to the system. The formulation of A/C composite does not leave more than 1% free lime, according to

Fig. 4-3 - Effect of density on corrosion resistance of cement-bonded materials (by example of sulphate attack)

the requirements of standards (40). However, the CEOCOR study (28) stresses that high lime, from high-cement content, helps to resist attack by acids.

In an investigation of the effect of adding up to 3% asbestos to concrete, Winer and Malhotra found that the asbestos reduced workability and required more water, which led to reduced strength, and inadequate performance (53).

To study the performance of an A/C matrix that was exposed to preliminary hydration, Berkovich et al evaluated the duration and level of shapeability of mixtures from portland cement with high (11%) vs. low (3%) C_3A content (54). The results are shown in Fig. 4-4.

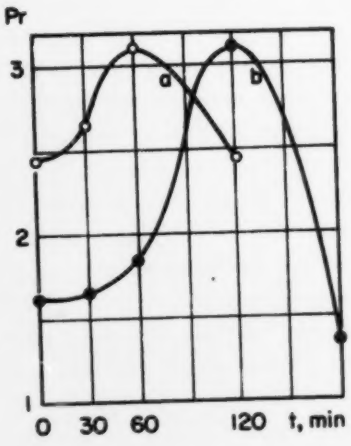


Fig. 4-4 - Shapeability curves of asbestos-cement relative to unity, for: a) high-aluminate portland cement from Spaskii and b) low aluminate portland cement from Sukholozhskii cement plants upon change of time of preliminary hydration of portland cement in the asbestos-cement suspension (54)

4.1.1.3 *Curing of asbestos/cement*

Some of the characteristics of results of curing HAC were reviewed in Section 4.1.1.1. Crennan et al developed a special procedure: a 24-h pre-cure at 30°C, then an 8-h autoclave cure at 175°C (29). Tests were made on concrete pads. Optimum conditions, including those for A/C pipe,

were yet to be determined at the time of testing (1963). The formulation included no silica, only normal proportions of HAC and asbestos. Greater corrosion resistance was obtained for autoclave-cured than for normal-cured products.

To clarify differing opinions, Quon and Malhotra investigated the curing of pure HAC and found that conversion to hydrates of cubic aluminate, independent of the W/C ratio, was greater at higher temperatures (50°C) (55). The highest strength was obtained for initially moist-cured (24 h, 21°C) one-year exposed specimens; this performance was followed by moist- or dry-cured (50°C) specimens.

In static laboratory exposure tests, Barbakadze et al established that autoclave-cured A/C was no more resistant to acid corrosion than normal-cured (38). The rate of attack was higher for the latter, but the final depth of corrosion was comparable.

The performance of normal- and autoclave-cured portland cements in carbonated water is very nearly comparable (Fig. 4-1).

The CEOCOR study states that density and compactness are generally lower for autoclave-cured than for water-cured products; however, their behaviour in aggressive media is again similar because of a higher chemical resistance of silica-carbonate binder (28). Contrary to some opinions, experience has not shown any significant differences between the type of production and resistance to attack by aggressive carbon dioxide and acids when using normal portland, low-calcium, and C_3A-free cement.

4.1.2 Design Considerations for Pipe and Distribution Systems

Kienow and Pomeroy have devised two methods, and charts for designing sewer pipes (56). They list four means of controlling the design of corrosion-resistant pipes:

- modify the pipe material
- increase the thickness, to provide for anticipated corrosion rate
- provide an inert liner
- use an inert material for the pipe.

Except for the last, all the designs are used in A/C pipes; the first has been reviewed in Section 4.1.1.

4.1.3 Protective Coatings and Linings

The corrosion of metallic and concrete piping led long ago to developing protective measures. Painted-on coatings, linings and deposited films are differentiated. Steel has been protected for more than 50 years with protective coatings and the accumulated experience has been directly transferred to A/C piping.

When pipes were introduced in the UK in 1928 both sides were coated (45). These measures were gradually omitted because of the good performance of A/C pipe, but with increased use in hotter climates, its performance had to be improved and specifications re-evaluated.

The use of protective coatings and linings is a passive measure, intended to separate the pipe's walls from aggressive environments which may or may not be controllable, therefore, the possible aggressive conditions must be carefully evaluated in the design stage (6). Under special conditions, specifications for A/C pipe require consultation with the manufacturer (28,40).

A considerable variety of materials are available as protective coatings but they are not always used advantageously. Springenschmid and Letsch have specified the following requirements for coatings (57):

1. high resistance to diffusion
2. good adhesion
3. no cracking with time or adverse change of mechanical and physical properties
4. additional resistance to stress from possible temperature changes

Trouble is often discovered only after the pipes are imbedded, as the literature reveals, when lining may not be possible.

4.1.3.1 *Application of protective coatings during manufacture*

Little can be added to Table 2-5 from the CEOCOR study (28) specifying protective coatings (Section 2.2). A detailed exposition is given of limiting concentrations of corrosive

agents whose use is permitted with both unprotected and protected pipe. Materials are suggested for exterior and interior protection; the preferences are: coal-tar, bitumen, coal-tar epoxy and epoxy.

A conservative limit of pH ≥ 6 is important for unprotected pipe exposed to corrosive media; limits for all coatings used are suggested as well. This must be compared with the currently valid ASTM specifications (40), and the newly proposed similarly conservative UK guidelines (46). The latter suggest a pH ≥ 6 be used with unprotected pipes and water containing less than 0.2% sulphates and a concentration of carbon dioxide of less than half the temporary hardness.

There is an important difference in the effectiveness of coatings used to protect A/C pipe against drinking water and sewage. In the first, and earlier case, bitumen is used most often, in several layers at 50-500 µm thickness (6). Coal-tar epoxy films, according to Kienow and Pomeroy, have served well for about 50 years (56).

Dekker presented data for water permeability of the most often used coatings (Table 4-4); for the least permeable, the time for saturation of concrete specimens was measured in decades (60).

The durability of asphalt-coated sewage lines ranges from excellent to poor. Barnes states that in Australia painted-on coatings are not favoured (58). For severe corrosion in a moderate climate, Eick suggests using pure or tar-epoxy coatings (20). Since failures occur with apparently thin or improperly applied coatings, the trend is to use two or more carefully applied layers on heated or unheated pipe, possibly with a primer, but without any solvents. Day (59) and others (46), warn of possible pinholes ("holidays") from evaporating solvents and stress the need for strict mechanical and quality control which eventually may lead to excessive cost, compared with pipes made from other materials.

Substituting one coating material with another without considering potential effects may prove troublesome as Yuskus revealed in the case of vinyl-lined (V/L) A/C pipe in Ashland, MA, USA (61).

In 1960, to correct an asphaltic taste in drinking water resulting from the protective coating in A/C pipe, a 70% vinyl solution in tetrachloroethylene (TCE) was used for coating the inside walls. More than 1000 km of this pipe was installed in the New England States. The chlorinated solvent did not dissipate before imbedding and water contained more than $40/10^9$ TCE, the suggested no-adverse response level (SNARL). Similarly high levels of TCE, not dissipated even after five years, were found elsewhere by Wakeham et al (62). A research program to study the problems consisted of first establishing a gas-chromatographic method for measuring TCE, then a thorough field evaluation of the conditions, and eventually, rehabilitation of pipe by relining. The latter is discussed in Section 4.1.3.2.

Table 4-4 - Permeability of organic coatings for water (60)

	Permeability g/cm^2 per day	Saturation time, 80 mm thick vibrated concrete
High frequency vibrated concrete 80 mm thick	$100 \cdot 10^{-4}$	2 months
Bitumen emulsion, 300 µm	$85 \cdot 10^{-4}$	2-5 months
Bitumen solution, 300 µm	$2.5 \cdot 10^{-4}$	6-16 years
Bitumen paint, 300 µm	$0.5 \cdot 10^{-4}$	35-88 years
Coal-tar epoxy, 300 µm	$0.7 \cdot 10^{-4}$	18-44 years
Solvent-free epoxy, 500 µm	$1.1 \cdot 10^{-4}$	15-40 years

Diederich summarized the requirements for no-paint, anticorrosive linings such as welded 2.5-mm soft polyvinyl chloride (63):

1. It must resist the influence of all waste water components and must reduce hydrogen sulphide corrosion.
2. It must fully satisfy the mechanical requirements of waste water systems, e.g., erosion, settling, cracks.
3. Attachment to the structure must be good, and permanent.
4. It must be insensitive to biological effects that occur in waste water systems.
5. The junctions of the lining must satisfy the same requirements.

Linings are increasingly used for difficult sewage situations; for a relatively modest cost they improve the serviceability considerably. However, they are usually not a part of the A/C pipe, which because of its smooth and dense surface, already provides a very resistant corrosion barrier.

4.1.3.2. *Application of protective linings after imbedding*

This is one of the more difficult operations but at the same time it is most acutely required. In most cases, water pipes have a diameter too small to permit entry of maintenance personnel; sewers are more often larger.

The problem of V/L A/C pipe releasing TCE into water has been successfully solved, according to Yuskus, by cleaning out the vinyl liner with wire brushes and then relining the pipe with an 8-9-mm layer of cement mortar, applied mechanically. A comparison of TCE content between the V/L and cement-lined pipe is shown in Table 4-5 (61). The TCE content was well within the suggested limits. Buelow et al also reported that A/C pipe had been rehabilitated with a similar technique (involving the deposition of calcite lining) (17).

For the repair of damaged epoxy linings of large sewers that would be too costly to exchange, Seyfried reported an improved technique

Table 4-5 - Comparison of tetrachloroethylene (TCE) content between vinyl- and cement-lined pipe (61)

Test No. Date Content changes per day	Supply ppb*	Piping System D (original condition) ppb	Piping system B (cement liner over vinyl) ppb	Reduction %
A-6 to A-13 9/19 - 9/26/80 one change	0.8	312.0	3.7	99
B-1 to B-6 9/29 - 10/10/80 two changes	0.4	179.0	0.4	100
C-1 to C-6 10/14 - 10/24/80 three changes	2.4	81.0	1.0	97
D-1 to D-6 10/27 - 11/7/80 four changes	1.0	26.0	3.4	96
E-1 to E-7 11/19 - 11/24/80 five changes	0.0	23.0	0.1	100

* ppb = part per billion (American)

Fig. 4-5 - Surface of an epoxy-resin coating, air sprayed with a solvent (1400X) (64)

for applying an epoxy-resin film (64). He showed, in electron microphotographs of surfaces, the effect of applying an epoxy-resin film, with and without solvent (Fig. 4-5, 4-6). In the former, the surface was distinctively cracked and thus could have provided an easy entry for corrosive fluids. He further cited the following requirements for successful relining:

- a layer of at least 500-600 µm
- airless application

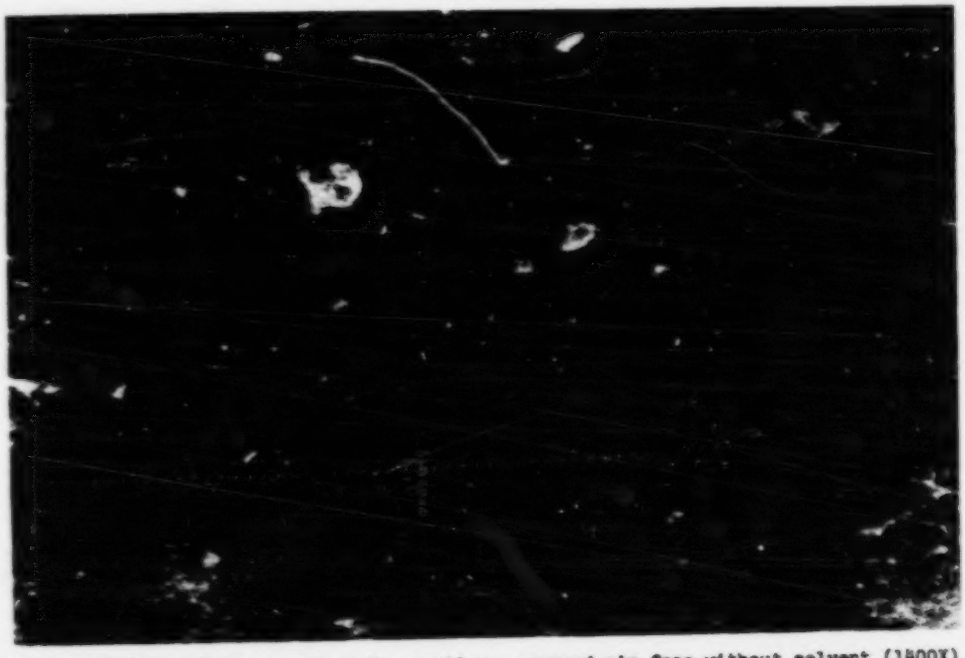


Fig. 4-6 - Surface of an epoxy-resin coating, sprayed air-free without solvent (1400X) (64)

- good adhesion to base
- predominantly smooth surfaces, achieved by sand-blasting and coating with special mortars, and smoothing.

On repair sites, further attack by the transported medium must be prevented by its proper treatment.

4.1.3.3. *Deposition of protective films from water after imbedding*

The deposition of protective films from transported water upon adding certain chemicals is a well-known technique long used for water treatment. It was first applied to combat corrosion of ferrous metal pipes, and its use extended naturally to A/C pipe.

As early as the 1960's, Eick spoke about the use of silicates and phosphates as protective additives (19). He was unable to confirm a manufacturer's claim of success for a silicate compound (Ferrosil), because no film was formed in corrosive water. However, phosphate in sufficient quantities did deposit a film once the solubility product of calcium phosphate was exceeded. At various times, other compounds, e.g., zinc oxide and zinc ortho- and poly-phosphates were tested. Lime is used most and under favourable conditions leads to deposition of calcium carbonate films. Merrill and Sanks have summarized and given detailed directions for its use (8).

Even from an undersaturated and oxygenated corrosive water, protective films formed from naturally-present inhibitors may at times be deposited. In his investigation of water in Amherst, MA, USA, Zajicek reported that iron and manganese compounds had been deposited in the pores, which protected the A/C surface against attack (65,66). Buelow et al came to a similar conclusion citing a highly corrosive water which surprisingly did not corrode the pipe, due to a deposited film of a rust-like substance (17). These natural inhibitors are often partially removed in the course of regular water treatment, making the water more corrosive (65). Kristiansen observed in his loop test of the water in Oslo, Norway, that a protective film of sludge formed from normally aggressive low-calcium, low-carbon dioxide water (67). Analysis of the film showed manganese, much iron, and silica and magnesium compounds. The corrosion of the pipe markedly increased during subsequent testing when the protective film was removed.

Lime has been continuously added for protection against "red" (rusty) water in the East Bay Municipality District (EBMUD) System in Oakland, CA, U.S.A. Stinson and Carns reported (68): "The District's long standing practice of pH adjustment of its treated waters ... by lime addition has protected A/C mains in the system from corrosion for 40 years. This conclusion has been confirmed by observing several sections of pipe removed from throughout the system. One typical section of A/C pipe, in the system about 41 years, had a thin protective coating and showed no erosion of the original pipe wall."

Deworm et al (69) investigated samples from seven water-distribution systems imbedded from 8 to 40 years. They found that A/C pipes were protected by a deposited greenish-brown film and were not corroded. The water was not aggressive.

The presence of iron and manganese compounds above a (low) permissible level affects water's taste and appearance unfavourably. Therefore, Buelow et al (17) and Schock and Buelow (5) investigated the effect of continuous addition of and film formation by a zinc compound, used in metallic pipes. Zinc is permissible up to 5 mg/L for humans, possibly less for fish. They worked out and documented an A/C pipe protection technique using 1 mg/L or less of zinc (as chloride or orthophosphate). Cost is comparable to that of fluoridation. The zinc compound film protects the A/C pipe from corrosion, but a deteriorated pipe cannot be rehabilitated by this technique.

Once a film is formed, the chemical chosen must be continuously added, otherwise the solubility product of the protective compound might again be unbalanced and cause dissolution of the film.

Since the formation of films involves water treatment, it is further discussed under Section 4.2.1.

4.2 CONTROL OF THE TRANSPORTED MEDIUM

4.2.1 Drinking Water Treatment

4.2.1.1 *Drinking water conditioning*

Most drinking water requires special treatment, that will ensure its quality in various respects, as presented in Table 2-2 (32). In addition, treatment is needed to protect water-distribution systems against corrosion.

Although much has been learned and applied in past decades, corrosion and its prevention are only now being based on sound theory. Therefore, water treatment and control have changed substantially in the past few years, mainly as a result of new knowledge in aquatic chemistry and of the availability of new tools for evaluating (25).

The largest difference is in the current understanding and measures for control of carbon dioxide. Waters with low calcium and alkalinity, i.e., undersaturated waters, preferably must be treated to saturation because they are very aggressive. Rational analysis of conditions and treatment requirements has now been simplified and water plants can be operated correctly and economically. Most often, water is treated with lime to deposit a calcium carbonate film. Merrill and Sanks give detailed information on procedures, therefore, only a few main points are discussed here (8).

Water conditioning requires the following procedures (8):

- identifying the saturation state of the unconditioned water;
- selecting the degree of oversaturation to be achieved;
- choosing the type of conditioning chemical or chemicals;
- adding the correct amount of each chemical to achieve the desired degree of oversaturation;
- determining the amount of $CaCO_3$ that can be formed during precipitation.

The conditions are chosen and followed by means of Caldwell-Lawrence diagrams, which are available for most commonly encountered temperatures and total dissolved solids contents of the waters treated (8).

For deposition of calcium carbonate films, the conditions given are (8):

1. The water should be oversaturated with $CaCO_3$. Oversaturation should be from 4 to 10 mg/L $CaCO_3$, i.e., the theoretical $CaCO_3$ precipitation potential should be 4 to 10 mg/L.
2. Calcium and alkalinity values should each be at least 40 mg/L $CaCO_3$ - more if economically feasible. They should be present in approximately equal concentrations.
3. The ratio alkalinity: $(Cl^- - SO_4^{2-})$ should be at least 5:1, in which all concentrations are expressed as mg/L of $CaCO_3$.
4. pH should be 6.8 to 7.3.
5. The water velocity should exceed 0.6 m/s.

Some of these conditions may be mutually exclusive, i.e., one may be achieved only at the expense of another. These guidelines are for metallic pipes. Little is documented for A/C for which the alkalinity: $(Cl^- - SO^{2-})$ is not critical because pipe is not subject to electro-chemical corrosion. For using diagrams, bulk-solution determinations of alkalinity, calcium and acidity are needed, as well as the water temperature and total dissolved solids.

Other tools for measuring the corrosiveness of water comprise: Langelier and Saturation Indexes, Ryzner Index (less used) and, particularly in Europe, Tillmans diagram. All are now outdated; they are discussed elsewhere and in the references.

Water treatment is a high-volume, recurring operation, therefore, economics is of great importance. In Table 4-6, costs for the most common conditioning chemicals are given (8). To condition a low-calcium, low-alkalinity water, such as one originating from snowmelts, would cost about 27 times that of normal water because two chemicals (lime and carbon dioxide) must be used.

A marble test is the most reliable means of determining the precipitation potential (saturation state) of water. Powdered calcium carbonate (marble) is left to react with the water. If the calcium concentration increases, the water is undersaturated; if it decreases, it is oversaturated; and if it doesn't change, it is at equilibrium.

Table 4-6 - Equivalent masses of some conditioning chemicals and approximate bulk chemical costs* (8)

Chemical	Equiv. mass chemical	Approx. chemical cost ¢/lb	¢/kg
CaO (quicklime)	28	2.25	4.95
$Ca(OH)_2$ (slaked or hydrated lime)	37	2.80	6.16
Na_2CO_3 (soda ash)	53	3.00	6.6
NaOH (caustic soda)	40	7.50	16.5
$NaHCO_3$ (bicarbonate of soda)	84	9.89	21.8
CO_2(carbon dioxide, commercial grade)†	22	4.10	9.02

*FOB Seattle, Jan. 1976

†Less expensive CO_2 can be obtained by generating CO_2 as a product of combustion

4.2.1.2 *Removal of asbestos fibres from drinking water*

Although preventing the release of asbestos fibres into water is the first aim of corrosion control, their removal if released is of much interest. It is also in the domain of water treatment.

A number of reports dealt recently with this problem on a laboratory scale. Lawrence et al have optimized the removal of asbestos fibres, using sand for filtration and iron compounds for flocculation. They were able to reduce the content of asbestos to below detectable limits ($<2 \times 10^4$ fibres/L) (70). Toft et al have reported that coagulation with filtration is effective for the removal of asbestos up to a factor of 300:1 (15).

A report on water filtration for asbestos-fibre removal is available through the U.S. Environmental Protection Agency (66), and a U.S. Patent was issued for removing asbestos fibres from water (71). The process is based on a bed of magnesium oxide, which retains virtually all fibres.

4.2.2 Waste Water Treatment

The treatment of waste water is much more difficult and less controllable than drinking water. However, as Barnes reported, even in such warm countries as Australia a satisfactory control had been achieved (58).

There are about 400 compounds present in waste water, at times exceeding the concentrations that will corrode A/C pipe. In addition, microbiological conversions of sulphur play a particularly prominent role in the degradation of A/C pipe (Section 2.3.4). Therefore, most of the effort is directed toward their control and reducing their effects. Since 1945, when Parker identified the thiobacillus action on cementbonded materials, many improvements were made, sometimes at great cost and after trouble developed with the attacked systems.

According to Barnes, the Melbourne ~40-year practice for the control of sewer corrosion is based on premises of carefully detailed design and management of the systems (58). He gave four main directives:

- minimize generation of hydrogen sulphide
- minimize emission of hydrogen sulphide
- minimize formation of sulphuric acid
- minimize the effects of sulphuric acid

He then elaborated each point in greater detail. The requirements were for concrete, but they inherently satisfy a number of the requirements of A/C pipe because it is technologically similar. A/C pipe has the following characteristics:

- hydraulic surfaces of high quality

- low permeability
- high-cement content
- uses sulphate-resistant cements
- highly alkaline reaction, normal in A/C

Wierig points out that only through full cooperation among planners, designers, technologists, and construction managers can resistant concrete structures be produced (72). Successful corrosion control is not only an isolated materials problem, as often implied; it is helped considerably by proper design and operating conditions. Eick stated that these operating conditions are not uncontrollable, because they depend on (20):

- regional position (climate, rain)
- design conditions (drops, house connections)
- oxygen content of waste water
- dilution
- flowrate and transport time
- chemical waste water treatment
- filling level of piping

Schremmer investigated in more detail the effects of temperature and concentration of hydrogen sulphide (73):

- Being microbiological, the process is very temperature dependent;
- At 18°C with higher hydrogen sulphide concentrations, the amounts of free sulphur formed and that bound in sulphuric acid were about equal. At lower concentrations, more sulphur was bound into acid, e.g., in a 12-week period, solutions of nearly 6% sulphuric acid were formed. At lower temperatures, noticeably more free sulphur formed. It was probably used in the formation of more sulphuric acid, but confirmation is needed. It might have been already provided in later investigations (Section 2.3.4.).

Eick specified conditions for reducing formation of hydrogen sulphide in waste water in Table 4-7, and for preventing its emission in Table 4-8 (20). Further, he showed data proving

Table 4-7 - Reduction of the formation of hydrogen sulphide in waste water (20)

- Oxygen enrichment in waste water by:
  - admission of fresh air
  - good ventilation and turbulence of the effluent level
  - rainwater, fresh water inflow
  - drops, house junctions, etc.
- Sulphate- and protein-content (nutrients) reduction by dilution
- Bactericides as addition
- Swift waste water transport, adequate slopes
- Temperature <10°C, prevention of inflow of warm waste waters

The formation of hydrogen sulphide is a function of temperature (optimum 27-39°C).

Below 10°C barely still a hydrogen sulphide generation. This increases, however, with increased temperature by:

- thermodynamically accelerated reaction rate
- livelier multiplication of bacteria
- negative solubility coefficient of oxygen in water:

  0°C: 14.2 mg O_2/L
  10°C: 10.9 mg O_2/L
  20°C: 8.8 mg O_2/L
  40°C: 6.6 mg O_2/L

Table 4-8 - Prevention of emission of hydrogen sulphide from waste water (20)

a)	Prevention of turbulence of already septic waste water
b)	Lower temperature (also hydrogen sulphide has a negative solubility coefficient; stronger emission at higher temperatures).
c)	Alkaline adjustment of waste water (the amount of undissociated hydrogen sulphide increases with decreasing pH value. Alkalies form HS -ions which are not emitted.
d)	Filling up of piping.
e)	Low turbulence inflow of septic and pressurized waste water into free-level piping.

the increased resistance of A/C pipe to acid (HCl) attack with time, but suggested protecting a new pipe with a coating.

In a systematic overview, Zietz reviewed all possible chemical treatments for the prevention of odour and corrosion (44). They are collated in Table 4-9, with a valuable cost comparison. Seyfried also presented a similar comparison. Technical oxygen is generally the most effective (64).

4.3 CONTROL OF THE EXTERNAL ENVIRONMENT

After imbedding, there is little possibility for change. Corrosive conditions of soil and groundwater must be carefully evaluated before choosing a particular pipe for laying, e.g., with or without a protective coating. Specifications and suggested protection for A/C pipe contain directives as to the environmental conditions under which a reasonably normal service may be expected (28,40,46). Permissible levels of acidity of soils, groundwater and transported water are given together with limits for sulphates, chlorides and other salts.

As a temporary measure for neutralizing acidic soils, Huenerberg and Tessendorff suggest adding alkaline materials, such as lime, into the ditch before laying the pipe (6).

4.4 USE OF BACTERICIDES

For controlling microorganisms, bactericides are added to any of three possible locations: the A/C pipe matrix, protective coatings, or to the transported medium.

Crennan et al have evaluated many bactericides for A/C formulations (29). They tested the following compounds with promising results:

- cupric oxide
- mercuric chloride
- quaternary ammonium compound
- phenyl mercuric nitrate
- salicylic acid
- ammonium molybdate
- tributyl tin acetate

However, when incorporated at concentrations of 0.1%, in test pads for laboratory exposure and in experimental sewer pipes in field tests, they showed no significant beneficial effect.

Best known is the bactericidal effect of coal-tar coatings, which have been used the longest (6,28,59). However, they must not be used inside the pipes for drinking water; the phenol components are not permissible because they decrease water quality.

Bactericides added to waste water are also effective to a degree but the practice is not recommended (20,44). Also effective are chlorobenzenes but according to Zeitz (44), their cost is much higher than other chemicals used for treatment (Table 4-9). Moreover, their use is not legally permitted.

Table 4-9 - Overview of methods for removing hydrogen sulphide from waste water (44)

Method	Action	Input point in a pressure piping	Established consumption in waste water	Suitable reaction conditions	Cost per m^3 of waste water German pfennig	Metering at 42 000 m^3 waste water per month and a sulphide content of 7.4 mg/L	Remarks
Use of hydrogen peroxide	Oxidation of hydrogen sulphide	10-20 min flow time before the end of piping	1.8 g H_2O_2/g H_2S	pH value ~7 Let to react in mole ratio 1:1 Prevent excesses	5.8	1.0 m^3 of 50% hydrogen peroxide	
Use of chlorine resp. chlorine-containing solutions	Oxidation of hydrogen sulphide	1-10 min flow time before the end of piping	3.4 g Cl_2/g H_2S	pH value ~8	4.6	7.6 m^3 of chlorine bleach	
Use of iron (II) sulphate	Precipitation of iron sulphide	At the end of pressure piping	8.3 g $FeSO_4.7H_2O$/g H_2S	pH value ~10	2.2	12.8 m^3 of saturated solution of iron (II) sulphate	The redox potential in waste water remains at a low level
Injection of pure oxygen into the pressure piping	Maintenance of aerobic conditions in the pipe	At the start of pressure piping	4500 m^3 O_2/mo. [calculated as per (9)]	- -	6.7 to 7.5	4500 m^3 O_2	
Use of emulsifiable chlorobenzenes	Suppression of sulphide-forming micro-organisms	At the start of pressure piping	≈85 g/m^3 waste water	- -	165	3.3 m^3 of solvex K	The introduction for commercial operation is according to environmental law forbidden. The use of the method is not recommended.

5. CONCLUSIONS

1. For seven decades, A/C pipe has served tens of millions of people around the world for reliable, efficient and inexpensive transport of drinking and waste water. In contrast, more than 15 million newborn to 4-year old children died in 1982, mostly because of lack of clean water, safe sanitation and medical care.
2. A/C pipe technology has been perfected and highly automated. Apart from the contained asbestos, the materials used are abundant, often locally available and inexpensive. In the manufacture of A/C pipe, strict compliance with the requirements of comtemporary cement technology leads to an efficient cement-bonded material. Its most important anti-corrosive property is its high density, which to a large degree prevents the intrusion of corrosive agents.
3. Like nearly all materials, A/C pipe is subject to several kinds of corrosion. In pressure pipe the most corrosive agent is soft water (calcium and carbonate contents are low). In sewer pipe sulphur is converted microbiologically to sulphuric acid, with subsequent acid corrosion and expansion of sulphate salts.
4. A new theory of corrosion by soft water recently evolved from the knowledge of aquatic chemistry. It revealed that previous measures of aggressivity of water were not correct, which often led to wrong conclusions and an improper use of pipe. A/C pipe behaves similarly to rocks at the earth's surface when they are exposed to water. If the water contains insufficient calcium to satisfy the requirements of the laws of chemical thermodynamics, the water will dissolve it from the solid phases, whether rocks or A/C pipe, with accompanying degradation.
5. The A/C matrix is corroded only in a thin layer at the surface, by a relatively small number of corrosive agents. In cases of prolonged and severe corrosion, asbestos fibres may be released, which may be of concern because asbestos can act as carcinogen in the respiratory tract. Epidemiological studies on the effects of asbestos possibly ingested with drinking water are difficult to make because of the complex methods of determination, the widespread presence of natural asbestos in waters, and lack of reliable long-term data on exposure of general population. Studies to date have not yet been able to establish unequivocally whether asbestos, if present in drinking water, is harmful to humans.
6. Several measures for substantially slowing down the corrosion of A/C pipe include modifications of the pipe or the transported medium. The pipeline environment (the ground) must be examined critically before because it cannot be modified after.
7. Long-term field tests for matrix modification of pressure and sewage pipe have shown that in durability high-alumina cements are much superior to normal portland and also to blast-furnace and supersulphated cements. Both the latter, as well, are superior to portland cements. Pressure pipes with C_3A - free cements were the worst. Contrary to general belief, the performance of standard water-cured pipe in aggressive drinking water is comparable to or even better than that of the autoclave-cured pipe. The former's high level of free lime, which in time forms carbonate, increases the resistance to degradation or at least provides much calcium. In the autoclave-cured pipe there is hardly any free calcium and therefore soft water attacks the calcium silicates in the A/C matrix immediately. They are however, more resistant to sulphate attack, a fact that might have obscured the correct conclusion until now. In high-alumina cements, the autoclave-cured pipes are also more resistant to degradation. Until now, no substitute material has been found which could match asbestos, in particular its homogeneous distribution in cement matrix.
8. Coatings are widely used to protect inside and outside surfaces of pipe. They are particularly important for protection against outside sulphate attack, which originates

from microbiological activities involving sulphur compounds in soils. Coal tars are the most effective coatings because of their bactericidal action, but they cannot be used with drinking water.

9. The inside corrosion of A/C pressure pipe can be slowed down relatively easily by deposition of certain compounds on pipe walls. The addition of lime increases the calcium concentration in water so that a protective film of calcium carbonate can be formed. The technique is widely used in water treatment plants. Various zinc salts and even some compounds of iron, silica and manganese behave similarly in natural waters. This film-deposition technique cannot rectify a badly damaged surface - special lining techniques must be used.
10. Corrosion protection of sewage pipes is the most difficult task involved in A/C pipe protection. It is particularly acute in warm climates. For its successful solution, cooperation among planners, designers, builders, and maintenance personnel is imperative. The management of fluid movement and aeration in correctly designed systems can prevent development of anaerobic conditions, which lead to massive microbiological activity, oxidation of sulphur and later build-up of sulphuric acid. Protective coatings are used as well. Among the available chemical treatments the introduction of technical oxygen is the preferred method. Bactericides, although costly, are logical protective agents; however, their use in some countries is not permitted.

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